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WADC TECHNICAL REPORT 58-13
PART 1

HIGH-TEMPERATURE INSULATION FOR WIRE

J. D. WALTON AND J. N. HARRIS
ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Project A 318

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WRIGHT AIR DEVELOPMENT CENTER

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January 31, 1958

Materials Laboratory
Contract No. AF 33(616)-3944
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Wright Air Development Center
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FOREWORD

This report was prepared by the Engineering Experiment Station of the Georgia Institute of Technology under USAF Contract No. AF 33(616)3944. This contract was initiated under Project No. 7350, Ceramic and Cermet Materials, Task No. 73500, Ceramic and Cermet Materials Development, and was administered under the direction of the Materials Laboratory WCRT, Wright Air Development Center, with W. T. Meuli and J. J. Krochmal acting as Project Engineers.

This report covers the period of work from 1 February 1957 to 31 January 1958. Principal personnel participating in this work included J. D. Walton, J. N. Harris, S. H. Fuller and J. D. Fleming.

ABSTRACT

A literature survey was undertaken to review possible methods for use in developing an electrical insulating coating for the high temperature protection of wire.

Ceramic-organic coatings were developed which cover the range from room temperature to 1300° F when applied directly to metal. These coatings withstand 1500°--but a wetting problem was encountered with the enamel on metals. However, since the final ceramic organic coating is applied over a base coating of aluminum oxide the wetting problem is not expected to cause difficulty. The effect of solution of aluminum oxide in the enamel is being investigated.

Curing studies have shown that methods of curing resin-frit coatings is an important parameter in obtaining proper burn-out temperature of resins.

Aluminum phosphate and silica were tested briefly as possible base coatings for the final ceramic-organic coating but adherence and corrosion problems caused this work to be discontinued.

Several anodizing baths have been tried, among them boric acid, oxalic acid, and sulfuric acid. Among these, sulfuric acid seems to give the best anodized coating.

Application of aluminum to copper wire has been the area where the most difficulty has been encountered. Although coatings with very good adherence have been obtained, first indications were that the problem in plating seemed to be in pre-cleaning of the copper. For this reason, gold plate was applied as an initial coating in some tests prior to aluminum plating the copper.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

RICHARD R. KENNEDY
Chief, Metals Branch
Materials Laboratory

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INTRODUCTION

As aircraft and guided missiles reach higher and higher speeds we run into the problem of the so-called "thermal barrier." This phenomenon results from an increase in friction between the skin of a plane or missile and the air. This friction produces a rise in temperature of the skin. Under these conditions severe service requirements are placed upon electronic components within the missile or aircraft.

This project was initiated on February 1, 1957 and has as its objective the development of wire insulation for application between -85° F and 1500° F. More specifically the wire should have the following properties:

1. High di-electric strength (400 V/mil and higher)
2. Low loss tangent (.01 and smaller)
3. Low di-electric constant (maximum 4.5)
4. Sufficient flexibility at room temperature to allow the coated wire to be wrapped around a mandrel 10 times the diameter of the wire
5. High impact strength
6. High abrasion resistance
7. Pressure-change resistant
8. Thermal shock resistant
9. Corrosion resistant to oils and salty atmosphere
10. Low strategic material content
11. Minimum weight
12. Maximum imperviousness to moisture
13. Maximum reflectivity
14. Concentricity of coating
15. Life expectancy of at least 10,000 hours

In order to carry out the objectives of Contract AF-33(616)-3944, the following line of experimental work was undertaken.

The development of a multilayer coating to incorporate the use of a ceramic-organic protective film and a refractory base coat obtained by precoating copper wire with an aluminum coating which will subsequently be anodized to aluminum oxide. This aluminum-oxide covering will greatly increase electrical properties at higher temperatures, as well as provide a good surface for the application of the ceramic-organic coating.

The ceramic-organic coating consists of an epoxy resin, ceramic frit combination used as a paint or coating. When the resin burns out, as the temperature is increased, the ceramic frit starts to fuse. After complete burn-out of the resin, the frit forms a coating which resists temperatures up to 1500° F.

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EXPERIMENTAL WORK

A. Preliminary Investigation

In order to carry out the objectives of Contract AF-33(616)-3944, a literature survey was undertaken to review possible methods available for developing an electrical insulating coating for the high-temperature protection of wire. This survey is included as an appendix to this report.

The references found in the literature survey are included in the bibliography. Only one reference was found to ceramic-organic coatings. This was "Development of Heat Resistant Paints" OTS Report No. PB111957, February 24, 1955, U. S. Department of Commerce. In this report some test data and formulations were given for a high-temperature heat-resistant paint containing ceramic components. The other references deal generally with methods and techniques of aluminum plating and anodizing. The anodizing references are included to provide a source of such information as the anodizing phases of this contract are developed beyond the present basic stage.

Since at the higher temperatures (1300° to 1500° F) the ceramic coating would be in a semi-molten condition, it is believed that an oxide coating beneath the ceramic-organic coating is highly desirable to maintain good electrical properties. Aluminum oxide, because of its ease of fabrication and good electrical properties was first considered for this purpose.

The best method of applying aluminum oxide as a uniform symmetrical coating on copper wire seems to be the anodization of an aluminum film previously applied to the wire. Numerous references to methods of aluminum film application and its subsequent anodization are listed in the bibliography.

The method of aluminum plating decided upon was that used by Couch and Brenner[2], and Connor and Brenner[3]. This method consists of the electrodeposition of aluminum from an aluminum chloride-lithium hydride-ethyl ether bath. This bath must be prepared in the absence of moisture and therefore it was necessary to construct a chamber for a dry, inert atmosphere.

Two other types of refractory base coatings were briefly investigated. These were aluminum phosphate and silica. Non-adherence and corrosive problems caused these investigations to be dropped.

B. Ceramic-Organic Coatings

1. Frit Resin Combinations

A possible ceramic-organic coating formula was selected from the OTS Report No. PB111957 (Table I), and an attempt to duplicate this formulation was made.

Table I Paint Formula from OTS Report

Component	Parts by Weight
Low melting frit	150
Medium melting frit	113
High melting frit	113
Chrome oxide green	56
Clay	62.5
Red iron oxide	4
Manganese Dioxide	1
Aluminum Stearate	3
Mica (325 mesh)	75
Dow Corning 806 Resin	270
Dow Corning 806 Resin	284
Butyl Alcohol	15
Toluol	25
Xylol	25

Several low temperature frit formulae were available in the OTS report. Two of these were smelted in our laboratory (Table II). Since no commercial frit reference numbers were given in the OTS report, substitutions of available frits believed to be in the proper temperature range were made (Table III).

Table II Low-Melting Frit Formulae[†]

Frit No. 1[††]	(%)	Frit No. 1C[††]	(%)
Borax	23.0	Borax	37.1
PbO	4.8	K-Feldspar	31.0
$NaCo_3$	3.8	SiO_2	11.4
$NaNo_3$	2.9	TiO_2	5.9
Fluorspar	4.8	Soda Ash	3.8
Cryolite	9.6	$NaNo_3$	9.0
$BaCO_3$	4.8	Fluorspar	.5
ZnO	4.8	Co_3O_4	.4
SiO_2	19.2	NiO_2	.9
K-Feldspar	22.0		
Co_3O_4	.2		

[†] OTS Report No. PB111957

[††] These frits were smelted at 1000° C

The formula was prepared by dry grinding each of the three frits separately for two hours in a one gallon ball mill charged with burundum balls. The other solids were then added and the whole solid mixture allowed to roll overnight in

Table III Frits Used in Formulating Ceramic-Organic Coatings

Low-Melting Frits (1000° to 1200° F)	Medium-Melting Frits (1200° to 1400° F)	High-Melting Frits (1400° to 1600° F)
XG-64 (Ferro)	231 O. Hommel	2903 (Ferro)
#1 (Table II)		2501 (Ferro)
#C (Table II)		
A1-5 (Ferro)		

At the time of these formulations these frits were believed to fall into the temperature range specified.

a ball mill using flint pebbles as the grinding and mixing medium. The solid mixture and part of the resin were mixed into a paste, after which the rest of the resins and the solvents were added. This liquid mixture was rolled in a jar with a few flint pebbles for complete mixing. Each formulation was tested by brush painting onto previously sandblasted steel plates. The coatings were cured at 600° F for one hour, then test plates fired at 100° intervals from 1000° to 1500° F.

These formulations gave very good coatings on air drying and after the 600° F cure, but above 1000° F, blistering and poor adherence was obtained. Since this was above the point where the silicone resin burned out, it was concluded that the trouble was in the ceramic components.

2. Ceramic Component Studies

Firing studies were made to improve coating properties between 1000° and 1500° F. Single frits and frit combinations were milled with water and Ferro Corporation L-389 Milling Compound, thus omitting the organic components so that a true study of the ceramic components could be made. A series of frits classified as low, medium and high melting (Table IV) were ground wet and dry, with mill additions and without, and mixed before grinding, as well as after. Also, the effect of adding titania, silica and mica in varying amounts were determined.

3. Formulation of Improved Coatings

The frits and combination of frits that gave the best results between 1000° and 1500° F were used in formulating a new series of ceramic-organic coatings. (Table V)

These coatings were an improvement over the first coatings but were still unsatisfactory. Major problems were lack of fusion in the low temperature range, and some blistering though not as severe as in the initial coatings.

Table IV Frits Tested in Frit Combination Study

Low-Melting Frits (1000° to 1200° F)	Medium-Melting Frits (1300° to 1500° F)	High-Melting Frits (1500° to 1800° F)
#1 (Table II)		2501 (Ferro)
#1C (Table II)	5836 (O. Hommel)	RN-721-F (Ferro)
3M (Minn. Min. & Mfg.)	5834 (O. Hommel)	15-M-1185 (Chivit)
231 (O. Hommel)		XG-201 (Ferro)

Table V Coating Formulations Used in Frit Combination Study

Constituent	Combination #1	#2	#3	#4
	(weight in grams)			
231 Frit	80	80	90	90
15-M-1185	20			
XG-201 Frit		20		
TiO_2			10	
Mica				10
SR-82 Resin	95.5	95.5	95.5	95.5
Thinner	34.5	34.5	21.5	34.5

4. Milling of the Coatings

A gelling problem was encountered when the resins were added to the solids. Therefore, it was decided to weigh out each coating and mill the ingredients together. This was achieved by first micropulverizing the frit to be used. The solids were weighed out and enough solvent added to just wet them. Resin was added until a fairly fluid charge was obtained. The charge was milled in a one quart mill half full of burundum balls. A milling study was made in order to determine the best length of time to mill the coatings. Coatings were milled various lengths of time up to 120 hours. Firing tests were run on each milled coating and 48 hours was selected as the best milling time. All of the coatings tested up to this time have been applied to steel plates by means of a brush. Some coatings that have been tested form gels when milled or when resin is added. This does not stop the application to metal plates by brushing. However, the best method for applying this coating to wire would be by spraying or dipping. This would automatically eliminate the use of any gelled coating.

5. Gel Formation Problems

Coatings milled and thinned to a spraying consistency with solvents did not gel. However, upon curing and firing, these coatings had a very chalky surface and resembled regular ceramic enamels before firing. Thinning the coatings with resin produced gels. Therefore, an investigation was made to find frits that would be compatible with the resin being used. A new resin, Dow

Corning 840, thought to be more compatible with ceramic frits than the G.E. SR-82 resin previously used, was obtained and tested. The resin reacted in exactly the same manner as the old resin. A number of frits were found that would not gel with either resin. Three frits used in the most promising coating listed in a supplement to OTS Report No. PB111957 were acquired from the O. Hommel Co. (Table VI). Several combinations of these three frits were tested in various combinations and with additions of lithium fluoride. Composition #9 in Table VII, containing 6 per cent lithium fluoride by weight produced the best coating to this

Table VI High-Temperature Resistant Paint

	Weight (g)
O. Hommel Frit #5476	77.5
O. Hommel Frit #3E46R	60.0
O. Hommel Frit #263	57.5
Chrome Oxide Green	27.6
China Clay	31.5
Aluminum Stearate	1.5
Mica (325 Mesh)	38.0
Resin	142.5
Mill for 50 hours, then add	
Resin	140.0
Butyl Alcohol	7.5
Toluol	12.5
Xylol	15.0

time. Initial fusion was at 1000° F and gave a smooth coating to 1500° F. Since only certain frits can be used without gelling, the possibility of finding a combination of frits which will fuse initially at 900° was somewhat limited. Additions of lithium fluoride up to 10 per cent caused a lowering of the initial fusion range below 1000° F but caused a greater incidence of high temperature defects.

Table VII Combination Study of Frits

Frit No.	#1	#2	#3	#4	#5	#6	#7	#8	#9
5674	79.5	60	66.7	50	100	130	75	50	50
3E46R	61.5	80	66.7	100	50	35	100	100	100
263	58.8	60	66.7	50	50	35	25	50	50
Lithium Fluoride								6	12

One hundred and ninety-six milliliters of SR-82 resin and thirty milliliters of thinner were used in the formulation of each test combination. These coatings were cured at 400° for one hour and fired to 1500° F.

6. Further Frit Resin Studies

The inability of the 5674-3E46R-263 frit mixture to produce a fused coat at low temperatures indicated that a study of the fusing ranges of a number of available frits would be desirable. Fourteen frits considered as ingredients of coating mixtures were tested according to the method of Kornbluth.[1] The approximate firing ranges are given in Table VIII. After classification of the frits in Table VIII into groups of low firing (< 1300° F), medium firing (1300° to 1400° F) and high firing (> 1400° F), compatibility studies were carried out on mixtures of the three groups. The frits were mixed in equal proportions and applied to steel plates. After firing to 1500° F with samples being removed at 100° F intervals, the samples were examined for frit reaction. No frit interactions were noted in any of the combinations studied. Frit combinations used were formulated using the G.E. SR-82 silicone resin with the 24 combinations listed in Table IX, with the exception of No. 6, 8, 12, 15 and 18, all of these mixtures formed a very tough gel which could not be thinned. The mixtures which did not gel were applied to steel plates and fired to 1500° F with samples being withdrawn at regular intervals. All coatings exhibited about the same behavior. The resin began to burn out at about 800° F and was completely burned out by 900° F.

Table VIII Approximate Firing Range of Frits

Frit Number	Manufacturer	Firing Temperature (°F)
5435	O. Hommel	1100
3M	Minnesota Mining	1100
3419	Ferro	1200
231	O. Hommel	1200
5674	O. Hommel	1300
3E46R	O. Hommel	1300
A1-5	Ferro	1300
5836	O. Hommel	1300
5834	O. Hommel	1400
270	Chicago Vitreous	1400
263	O. Hommel	1400
5837	O. Hommel	1400
15M1185	Chicago Vitreous	1500
XG-201	Ferro	1500

Frit combinations No. 1 through 18 were mixed with the Shell X-131 Epoxy resin. Mixtures No. 1, 3, 7, 8 and 9 formed gels. Steel plates were sprayed with the remaining mixtures and fired in the usual manner. Formation of bubbles was noted in all samples at low temperatures about 400° F. Upon being thinned with acetone before spraying, the mixture did not form bubbles until a temperature of about 1200° F.

Table IX Frit Combinations Investigated

Mixture Number	Low Firing	Medium Firing	High Firing
1	3419	3E46R	15M1185
2	231	3E46R	15M1185
3	3M	3E46R	15M1185
4	3419	5674	15M1185
5	231	5674	15M1185
6	3M	5674	15M1185
7	3419	3E46R	263
8	231	3E46R	263
9	3M	3E46R	263
10	3419	5674	263
11	231	5674	263
12	3M	5674	263
13	3419	3E46R	5837
14	231	3E46R	5837
15	3M	3E46R	5837
16	3419	5674	5837
17	231	5674	5837
18	3M	5674	5837
19	5435	3E46R	15M1185
20	5435	5674	15M1185
21	5435	3E46R	263
22	5435	5674	263
23	5435	3E46R	5837
24	5435	5674	5837

Two new epoxy resins were secured from the Haveg Corporation (#66 and #67); these resins had the highest burn out temperatures of any resins tested and their compatibility with frits was better than previous resins.

To expedite the testing of frit-resin coatings a temperature gradient furnace was constructed. The furnace consists of a 12-inch alumina tube 1-1/2 inches in diameter placed in a vertical position and closed on the bottom end. The tube is wrapped with Kanthal resistance wire in such a manner as to cause a drop in temperature of approximately 100° F for each inch of tube length. The power supply is 110-V AC and is controlled by a variac. The temperature of the lower end of the tube is maintained slightly above 1500° F and the upper end at approximately 400° F. Temperature is measured by 12 thermocouples in the tube spaced 7/8 inch apart, starting 7/8 inch from the bottom of the tube. The thermocouples are connected to two 12 position switches which are, in turn, connected to a Wheelco potentiometer. The temperature at any point in the furnace can be determined by plotting the temperatures recorded from the 12 thermocouples (see Figure 1). Firing of frit-resin coated metal strips in this furnace has revealed defects in the coatings that were not observed in previous step-wise firings.

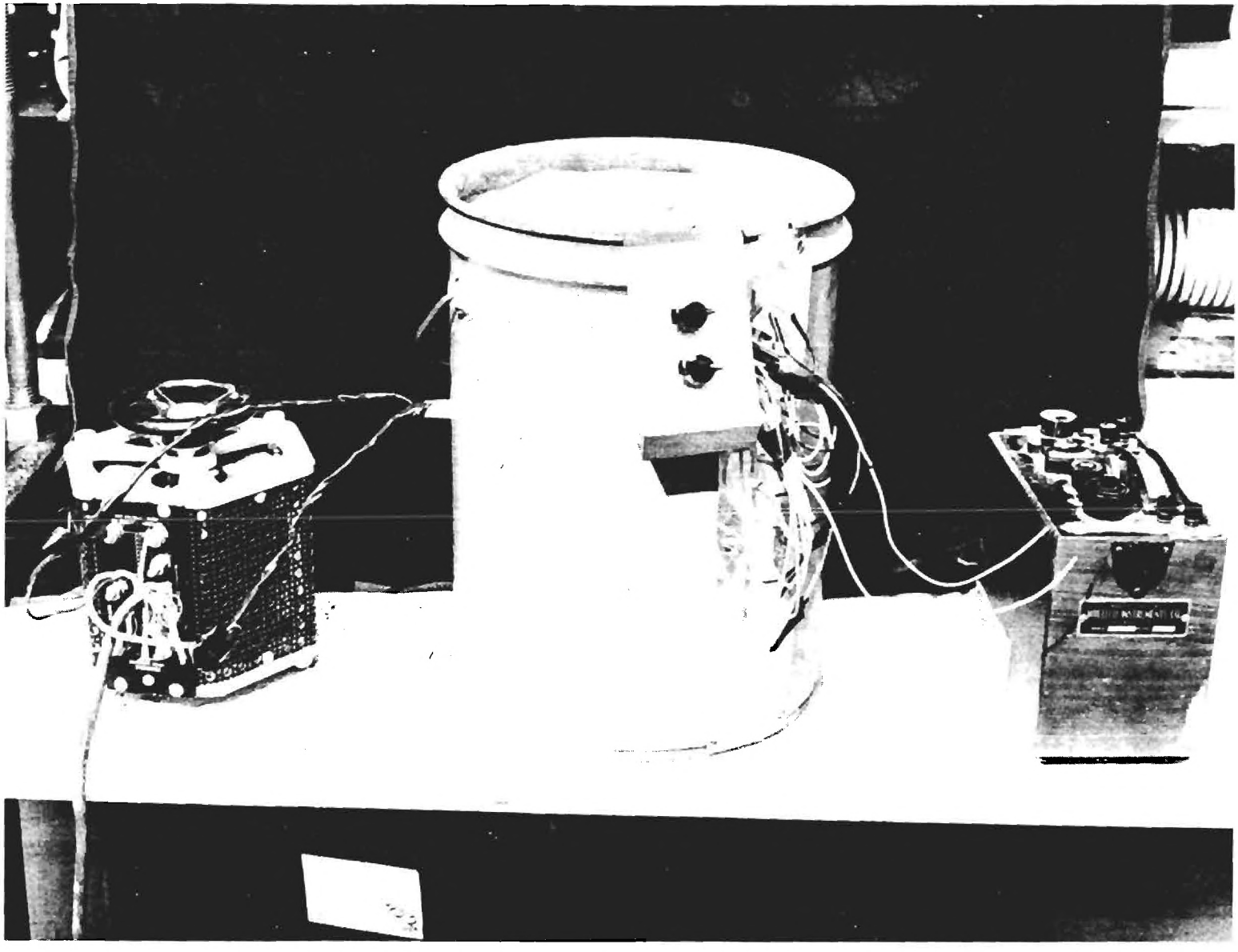

Figure 1. Temperature Gradient Furnace.

Figure 2 shows coated strips using combinations of O. Hommel's 231 and 263 frits. This print shows the effect of addition of high firing frit (263) to a low firing frit (231). 2C is 100 per cent 231, 2B contains 15 per cent 263 and 2A contains 35 per cent 263. The same resin frit combinations as above were cured at a slightly higher temperature for a shorter period of time. When these strips were fired, all three combinations showed resin burn out. A curing study on frit resin combinations is now in process. Figure 3 shows the effect of time on curing frit resin samples. Sample A was cured for 15 hours, B for 24 hours and C for 36 hours at 200° F. Figure 4 shows the effect of temperature on curing. Sample B was cured for 15 hours at 200° C and A was cured for 2 hours at 450° C.

The frit resin combinations now being tested gave continuous coatings to 1300° F, above 1300° the coatings have not burned off but bead up and do not wet the metal. It is felt that these coatings will wet an aluminum oxide coating, however.

Tests are now being conducted to determine the effect of solution of aluminum oxide in the enamel glasses being used and the wetting effect of these coatings on an aluminum oxide coating.

C. Base Coatings

1. Initial Investigations

Due to the nature of enamel glasses, poor electrical properties are obtained from the ceramic-organic coatings in the range of 1500° F. A ceramic coating which begins to fuse at 1000° F will be of necessity in a viscous liquid state at 1500° F and will act as a conductor. For this reason, some sort of refractory base coating is needed to act as a stand-off insulator and maintain good electrical properties.

Tentative investigations were begun using alumina and phophoric acid in the composition shown in Table X. The reactants were mixed and milled in glass jars and sprayed onto steel and copper plates. The steel plates were severely attacked by the phosphoric acid. The copper plates were cured at 650° F for 3 hours. Sample No. 3 had very good adherence; Sample No. 2 fair adherence; and Sample No. 1, poor adherence. After curing, the samples were heated to 1200° F

Table X Phosphate Bond Compositions

Mixture Number	Alumina (%)	85% Phosphoric Acid (%)
1	80.0	20.0
2	70.2	29.8
3	54.2	45.8

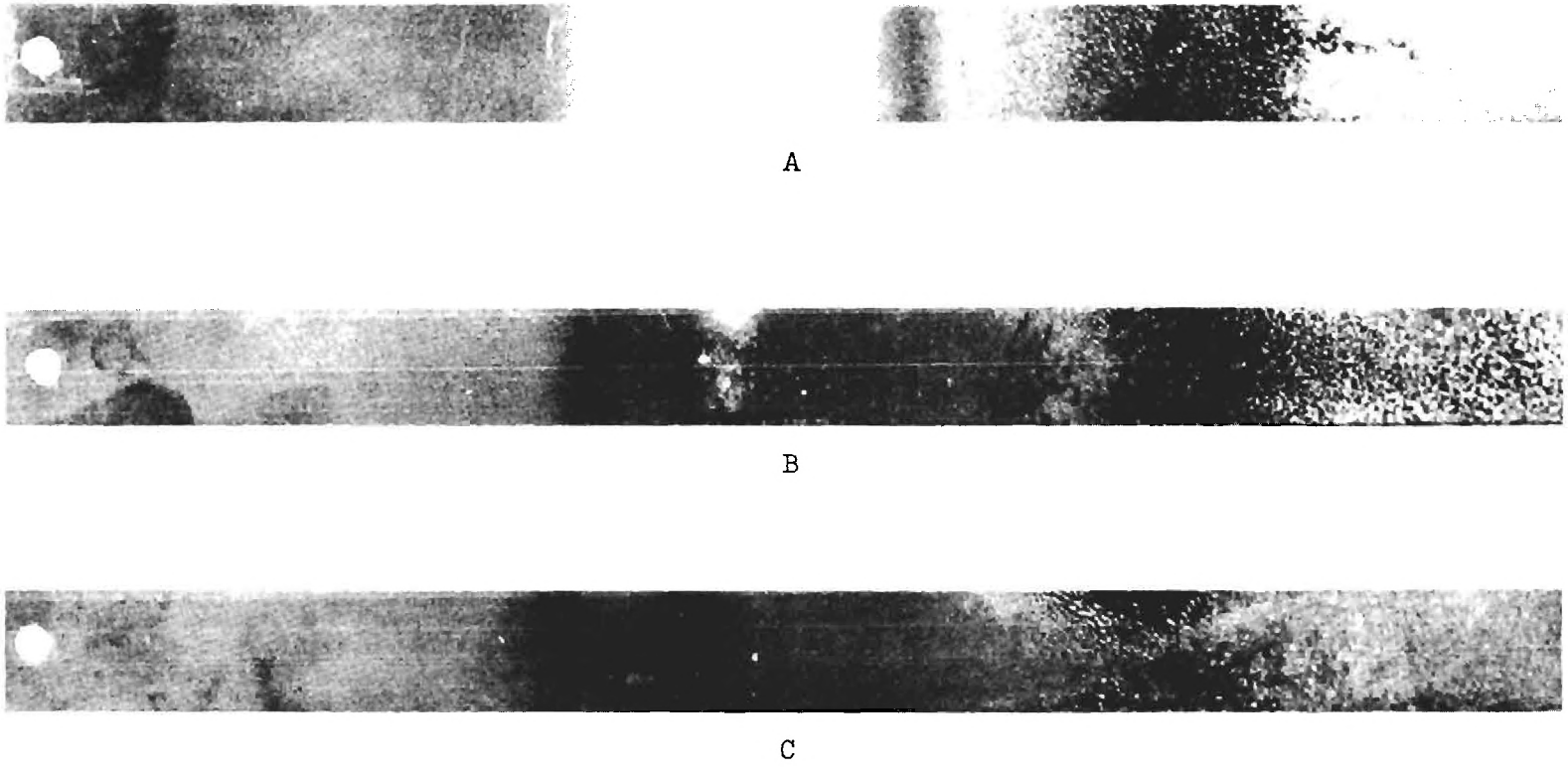

Figure 2. Frit Resin Coated Strips Fired in Gradient Furnace.

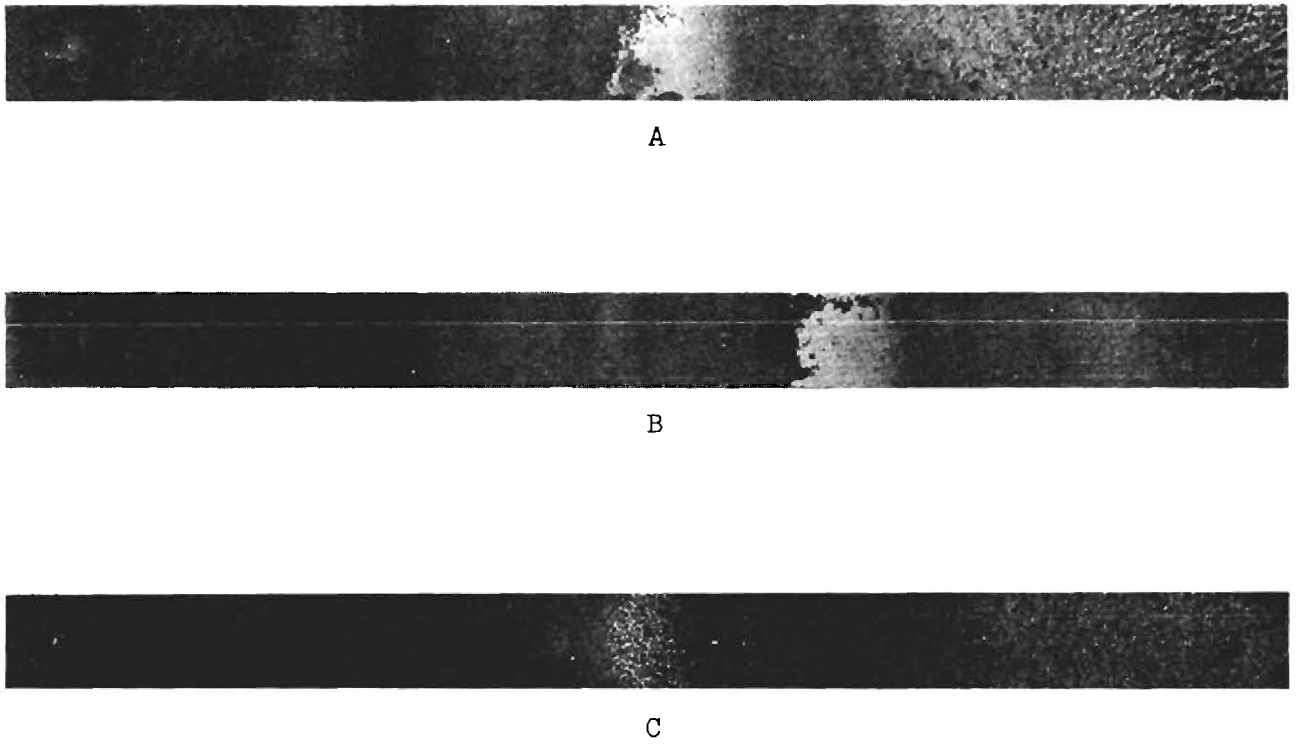

Figure 3. Effect of Time on Curing Frit Resin Samples.

A

B

Figure 4. Effect of Temperature on Curing Frit Resin Samples.

where the coating separated from the copper substrate. Steel represents a more satisfactory substrate than copper for coating investigations because of its lower thermal expansion. For this reason, attempts were made to inhibit the phosphoric acid attack on steel. A sample of Rodine inhibitor was obtained from the American Chemical Paint Company and added to the 85 per cent phosphoric acid to form a 1 per cent Rodine solution. A mixture of 10 per cent of this phosphoric acid solution with 10 per cent hydrated alumina, 80 per cent alumina grain and 1 per cent ammonium fluoride, as a further inhibitor was compounded. These coatings came loose from the substrate when fired.

A second possibility for providing electrical resistance is the use of a refractory anodized aluminum undercoating. Coatings of aluminum have been deposited on copper by electroplating from a lithium aluminum hydride-ethyl ether bath. These coatings can be anodized by any of the common anodizing methods. This seems to be the best procedure for obtaining a uniform symmetrical coating of aluminum oxide on wire.

2. Construction of the Dry Box

Since the lithium aluminum hydride bath must be prepared and used in a neutral atmosphere, construction of a dry box was carried out. (See Figure 5) The box consists of a stainless steel tank which has been fitted with four glove ports and a braced lucite cover. A Kinney high vacuum pump is used to evacuate the chamber prior to filling with dry nitrogen. An entrance port 10 inches in diameter and 12 inches long has been added to the box. The entrance port consists of a stainless steel tube in the side of the dry box with a cover on the inside and outside. Items to be placed in the dry box are placed in the port and the outside cover closed. The port is then purged with dry nitrogen 4 times and the inside cover removed. This facilitates the operation by allowing items to be removed from, or placed in the chamber while it is in operation. A 14-28 volt D.C. motor generator set is used as the current source for plating. For safety reasons the dry box is located in separate laboratory facilities. All controls are located in one central control panel allowing one man to control the plating operation. (See Figure 6)

3. Operation of the Dry Box and Plating Procedure

All items necessary for mixing the plating solutions are placed in the dry box and the box closed. The box is evacuated to 15 inches of mercury and filled with nitrogen 4 times.

The plating solution used is a 3 molar aluminum chloride 0.4 molar lithium aluminum hydride solution made up directly in the plating vessel from solutions of 5 M aluminum chloride in ether and lithium aluminum hydride in ether. These solutions are made in the dry box from anhydrous aluminum chloride and lithium aluminum hydride, using sealed cans of anhydrous ether opened inside the box.

In preparing the bath extreme care is necessary to be sure that no moisture enters the bath. Difficulty was encountered in obtaining anhydrous aluminum

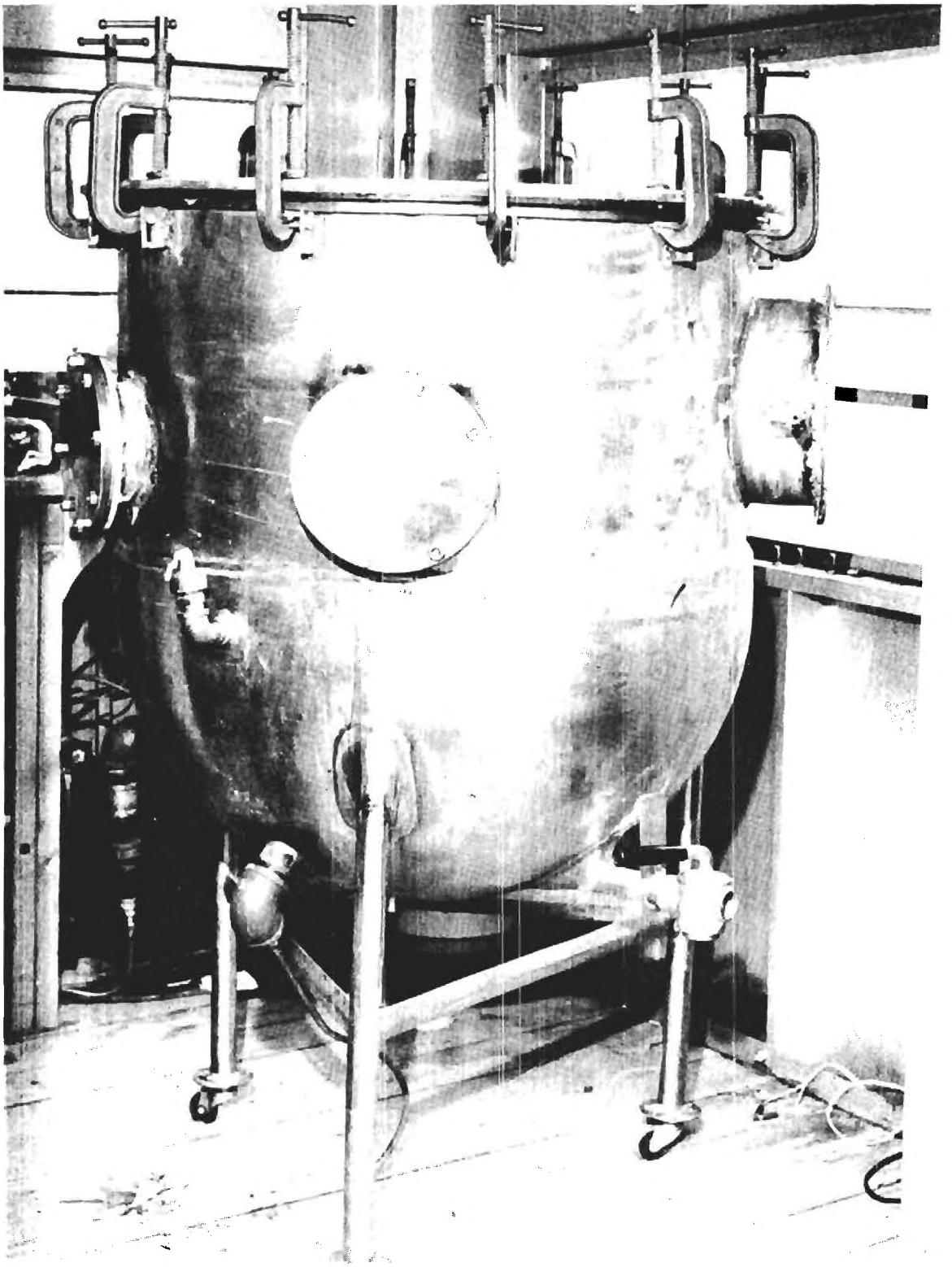

Figure 5. Dry Box for Aluminum Plating.

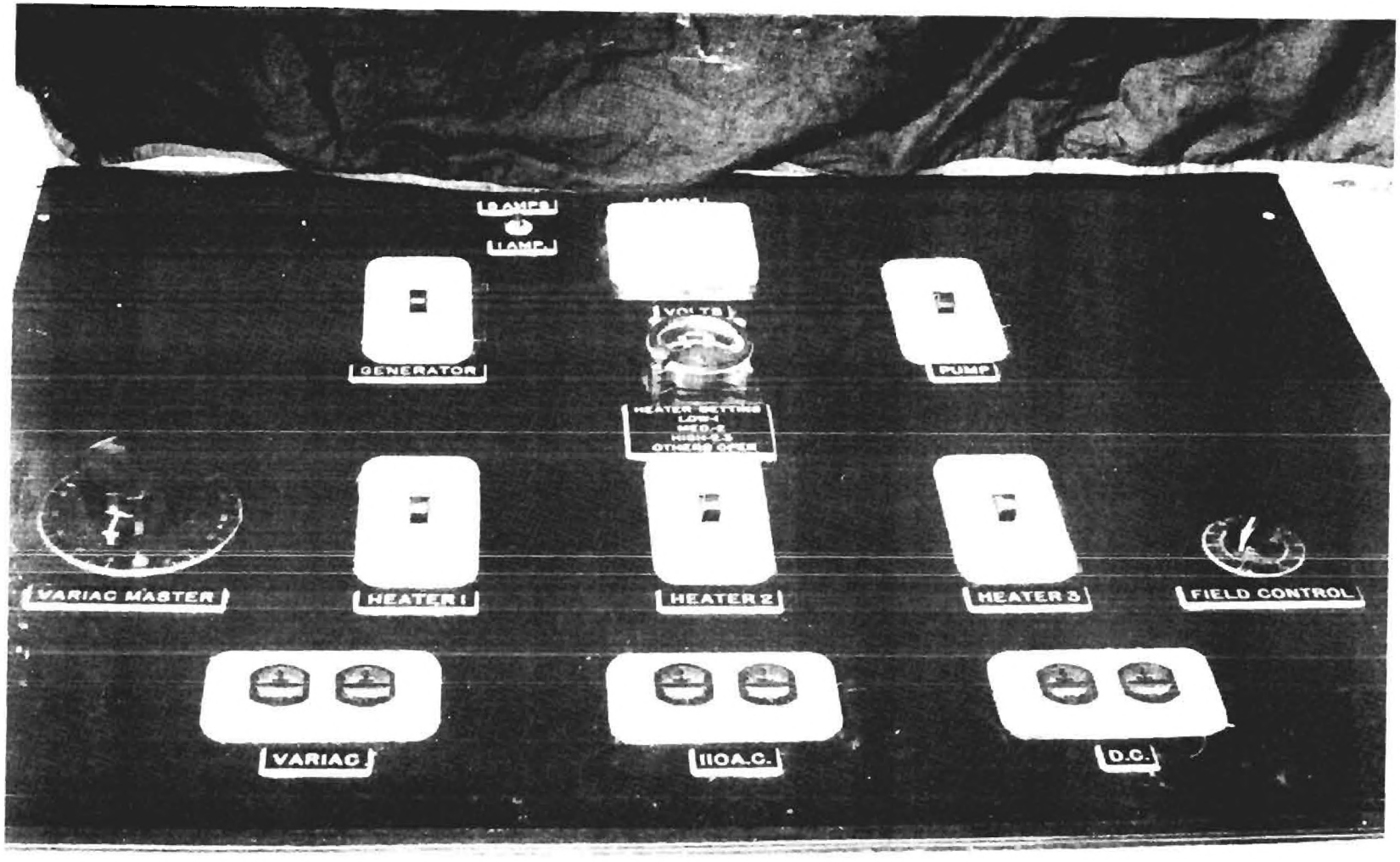

Figure 6. Control Panel for Dry Box.

chloride. One batch of aluminum chloride was received in unsealed jars and could not be used. It was also found necessary to use sealed cans of anhydrous ether and to open these inside the dry box. Care also had to be taken to make sure the inside of the dry box was clean since spilled salts tended to pick up moisture when the box was open and would tend to hold moisture while the box was in operation. This problem has been greatly reduced with the addition of the entrance port. Bath life has been greatly increased since it is not necessary to open the dry box.

Some copper plates were plated with aluminum from baths that contained some moisture. These plates on standing would pick up moisture and become sticky and the aluminum coating could be easily rubbed off. It was found that this problem could be eliminated by washing the plates with concentrated sulfuric acid immediately on removal of the test plate from the plating solution.

A major problem in obtaining a good coating on copper is in the cleaning procedure. The cleaning procedure used for copper plates is the same as that used by Connor and Brenner[3] and is as follows.

(A) Bright dip in hydrochloric acid - nitric acid - sulfuric acid - water, 1:38:78:10

(B) Dip in 5 per cent sulfuric acid containing 2 per cent hydrogen peroxide

(C) Rinse in water and dry

(D) Immerse in ethereal solution of salicylic acid for 10 minutes.

It was thought that it might be possible to get around the difficult cleaning procedure by preplating the copper with another metal less subject to oxidation. A gold plating solution not requiring electrolysis was acquired from Baker and Company. The aluminum plate did not adhere as well to the gold as to the copper, however.

Aluminum has been plated on copper wire of several sizes. Severe bending of this wire has produced no visible spalling or cracking.

Tests are now underway to determine the best current density, time and method for obtaining a uniform aluminum coating. Of the operations used in the multilayer coating process the aluminum plating operation has been the most difficult.

Aluminum is presently being applied to copper wire for subsequent anodization, and application of a ceramic-organic cover coat. (Figure 12) The aluminum coatings obtained thus far have produced no visible spalling or cracking when subjected to severe bending. These coatings are being anodized (Figure 13) and will be submitted to all physical tests called for by the contract. Samples are also being prepared to be submitted to the University of Illinois for electrical measurements.

4. Anodizing Techniques

Several anodizing techniques are presently being tested. The apparatus used for anodizing is shown in Figure 7. Efforts are being made to obtain a coating similar to that of the Permaluster Process which is presently being used to protect wires to 1000° F. Of the methods tested, the sulfuric acid anodizing process most closely resembles the Permaluster Process. Figure 8 is the Permaluster coated wire and Figure 9 is anodized wire using a sulfuric acid bath. Boric acid and oxalic acid baths are also being tested. See Figures 10 and 11. Samples of these anodized wires will be prepared and sent to the University of Illinois for electrical measurements.

DISCUSSION

A. Frit Resin Combinations

Work with the frit resin combinations indicated that an epoxy resin is best suited for use in the coatings since its burn out temperature is about the same as that of the silicone resins and its compatibility with frits is significantly higher.

Curing studies point up the fact that curing is a significant variable and further studies along these lines are needed. The Haveg resin now in use appears to have a high enough burn out temperature to produce a continuous coating with present frit combinations, however, in the range of 1300° to 1500° F the ceramic coatings do not wet the metal strips properly. Frit combinations applied alone (that is not containing resins) give a smooth coating in this region. Therefore, it is concluded that the combination of the resin and frits causes the non-wetting in the 1300° to 1500° F range. Curing studies completed at this time show that cures at higher temperatures and for long periods of time decrease this non-wetting tendency. It is felt that this tendency may be reduced further when the coating is applied to an aluminum oxide base rather than metal.

B. Base Coatings

The anodized aluminum base coating seems to be the most promising at the present time although the studies of this coating are far from complete. Anodized coatings 0.00015 inch thick have been reported to have flexibility sufficiently high to allow the wire to be bent around a radius only three times the diameter of the wire without crazing or fracturing the film. The one limiting factor appears to be the hygroscopic nature of such a coating which in the presence of moisture might cause the di-electric strength to be reduced considerably. The sealing ceramic-organic coating should eliminate this difficulty, however.

FUTURE WORK

Work planned for the immediate future has been divided into the following categories.

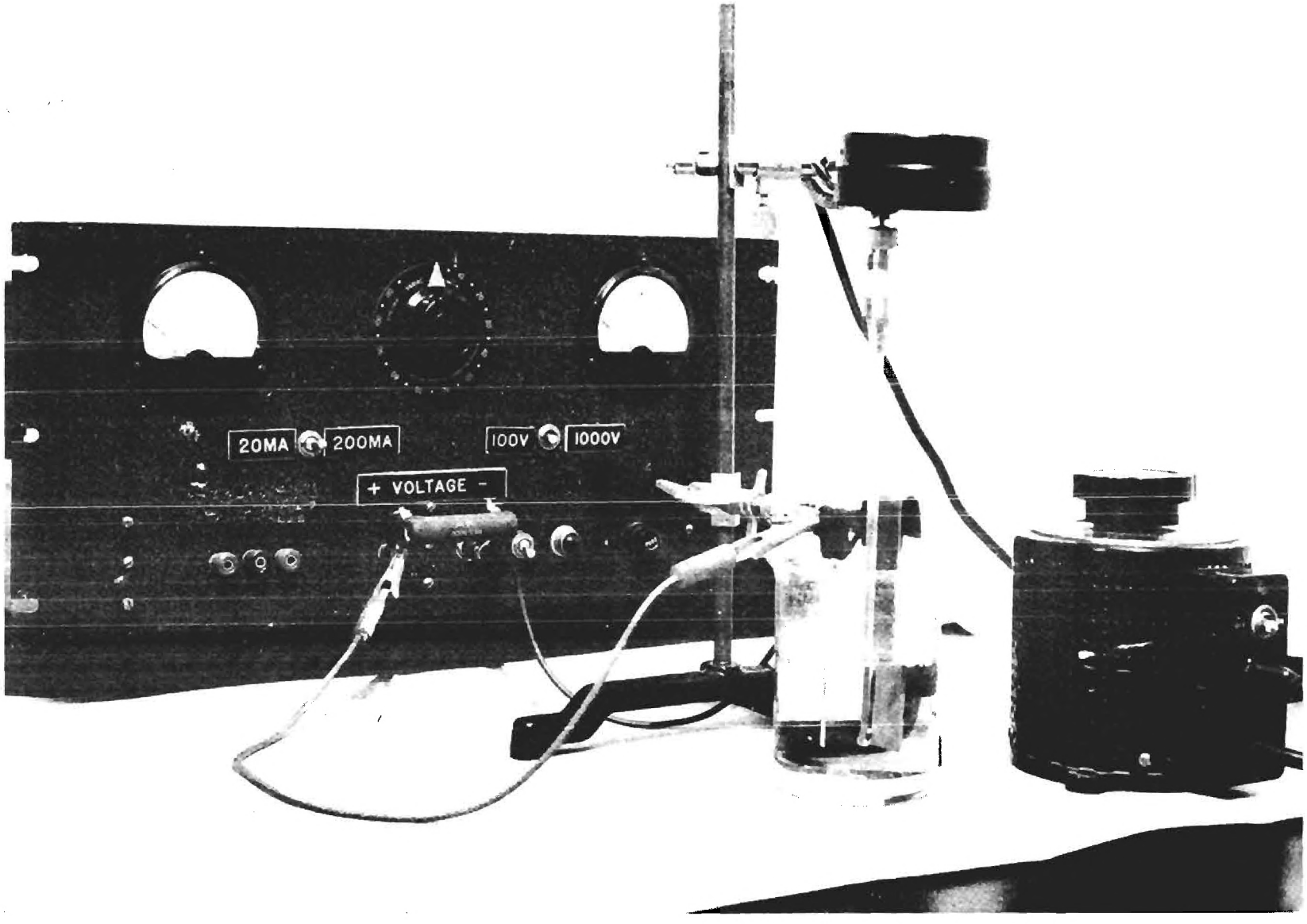

Figure 7. Apparatus for Anodizing Aluminum.

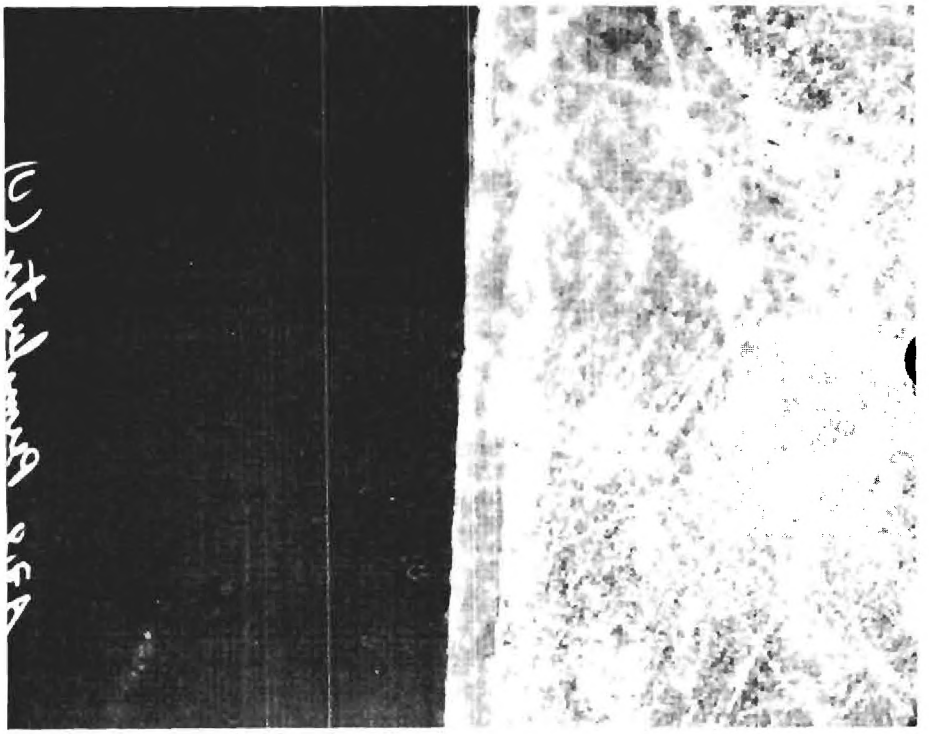

Figure 8. Micrograph of Anodized Permaluster Wire. (325x)

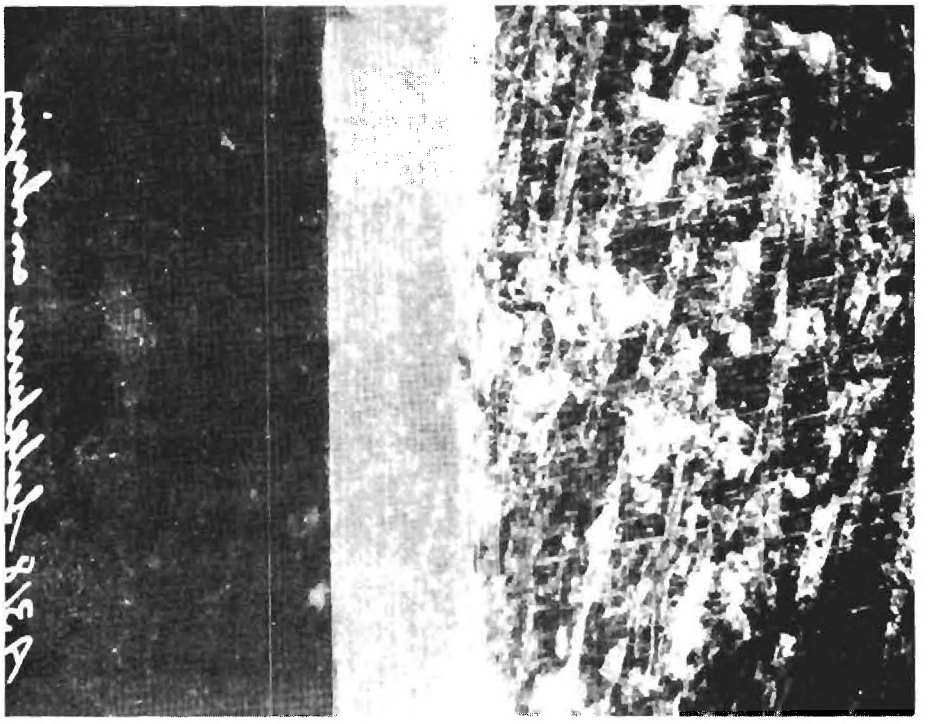

Figure 9. Micrograph of Sulfuric Acid Anodized Aluminum Wire. (325x)

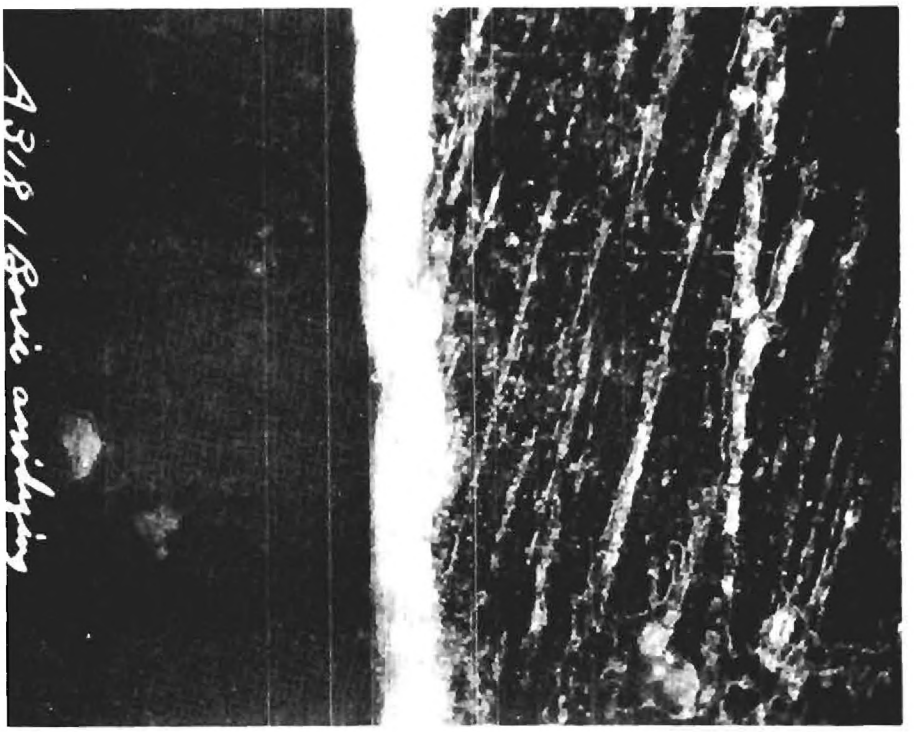

Figure 10. Micrograph of Boric Acid Anodized Aluminum Wire. (325x)

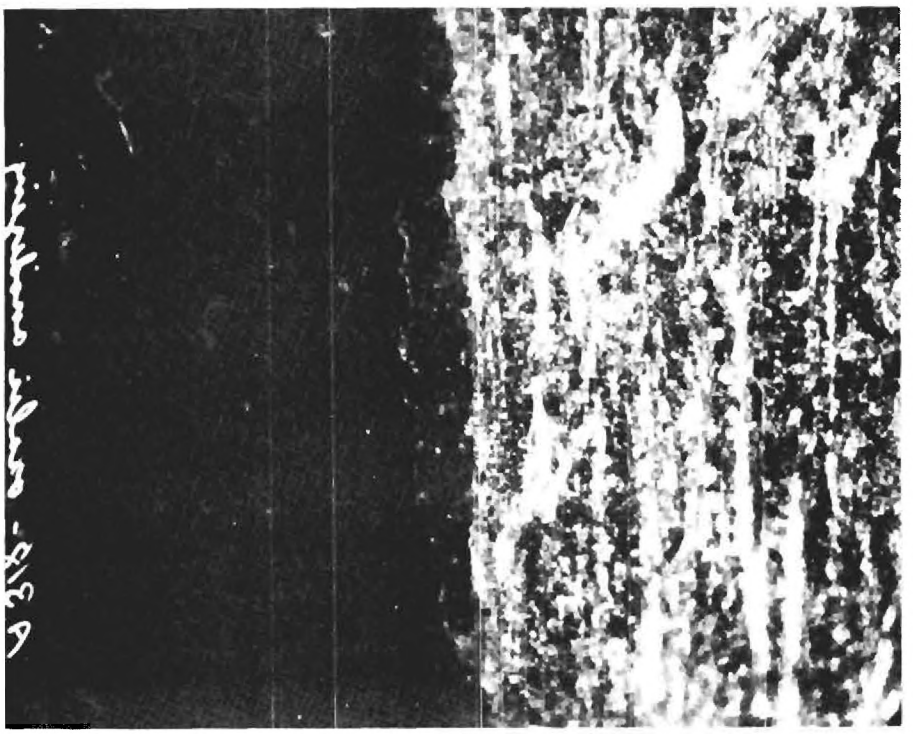

Figure 11. Micrograph of Oxalic Acid Anodized Aluminum Wire. (325x)

Figure 12. Micrograph of Aluminum Plated Copper Wire.

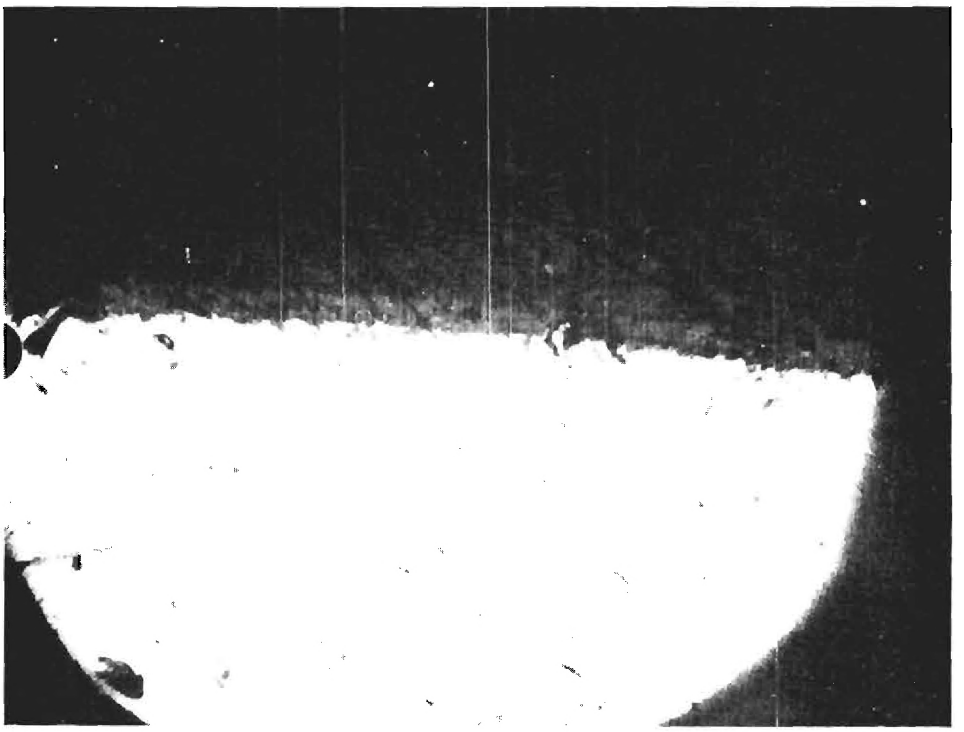

Figure 13. Micrograph of Anodized Coated Copper Wire.

A. Ceramic-Organic Coatings

Further work on the improvement of ceramic-organic coatings as a sealer for the crystalline base coatings will be continued.

B. Aluminum Oxide Coatings

Aluminum coatings will be applied to copper, iron and inconel substrates with emphasis on developing maximum density and adherence. These coatings will be anodized by several of the commercially practiced processes. Such variables as current density, anodizing bath, bath temperature and anodizing time will be related to porosity, flexibility and electrical properties in order to establish the type of anodized coating required.

C. Colloidal Silica

Studies will be initiated to determine the sealing properties of colloidal silica used to impregnate anodized coatings. Such variables as colloidal silica particle size, stabilizing agent, gelling agent and concentration will be studied in relation to the degree of infiltration obtained and effect on flexibility. The hygroscopic nature of the deposited silica after heating to 1100°-1500° F will be determined.

D. Wire Coatings

Experimental coatings will be applied to wire of 0.075, 0.060 and 0.020 inches in diameter and will be evaluated for physical and chemical properties.

BIBLIOGRAPHY

1. Murray Kornbluth, "Development of Heat Resistant Paints," OTS Report No. PB111957, 24 February 1955, U. S. Department of Commerce.

2. D. E. Couch and Abner Brenner, "A Hydride Bath for the Electrodeposition of Aluminum," J. Electrochem. Soc. 99, 234-244 (1952).

3. J. H. Connor and Abner Brenner, "Electrodeposition of Metals from Organic Solutions," Part II, "Further Studies on the Electrodeposition of Aluminum from a Hydride Bath," J. Electrochem. Soc. 103, 657-662 (1956).

4. A. Jenny, The Anodic Oxidation of Aluminum and Its Alloys, Charles Griffin and Company, Ltd., 1940.

5. R. M. Bivins and W. W. Bradley, Protective Coatings for Metals, Reinhold Publishing Corporation, Chapter 3, 1955.

6. F. R. Collins, "Aluminum Electroplated on Steel from Fused Salt Bath," The Iron Age, January 17, 1952.

7. R. F. Hafer, "A Talk on Anodizing," Reynolds Metals Company, Engineering Services Department, c/o General Sales Office, 2500 South Third Street, Louisville 1, Kentucky.

8. "Finishes for Aluminum, Section Two, Standard Processes," Technical Editorial Service, Reynolds Metals Company, Inc., Louisville 1, Kentucky, 1946.

9. "Alumilite Hard Coatings," Aluminum Company of America, Alcoa Finishes, Bulletin No. 5, January 1952.

10. "Martin Hard Coating," Aluminum Company of America, Alcoa Finishes, Bulletin No. 5, January 1955, U. S. Patents 2,692,851 and 2,692,852.

11. "Instructions for Applying Alcoa Alumilite Finishes," Aluminum Company of America, Pittsburgh, Pennsylvania, 1956.

12. Chuff, G. W., U. S. Patents 1,068,410 and 1,068,411, July 29, 1913; Presser, U. S. Patent 1,117,240, November 17, 1914.

13. R. M. Burns and W. W. Bradley, Protective Coating for Metals, Reinhold Publishing Corporation, p. 652, 1955.

14. K. G. Compton and A. Mendizza, "Electrical Breakdown of Anodically Oxidized Coatings on Aluminum: A Means of Checking Thickness of Anodized Finishes," Papers on Anodic Coatings, American Society for Testing Materials, Philadelphia, Pennsylvania, Vol. 40, 1940.

15. Metco News 8, No. 2, Metallizing Engineering Company, Inc., 1101 Prospect Avenue, Westbury, New York

The following section of this bibliography was secured from the Reynolds Metals Company, and covers recent literature on the subject of anodized coatings.

16. "Effects of Air Agitation in Sulfuric Acid Anodizing," Metal Finishing 51, No. 3, 78-81 (1953).

17. K. J. Van de Loo, "Review of Processes for Anodizing Aluminum," Polytech. Tijdschr. I, 514a-18a (1952).

18. "Physical and Chemical Properties of Anodic Coatings," S. Wernick, Sheet Metal Industries 29, 1027-36, 1040 (1952).

19. "The Nature and Properties of the Anodic Film on Aluminum and its Alloys." H. W. L. Phillip's (British Aluminum Company, Gerrands Cross, Bucks, England) Symposium on Properties of Metallic Surfaces. (Inst. Metals, London) 1952, 237-52.

20. "Anodic Oxidation of Aluminum in Sulfuric Acid," Tomashov. and Tyukina. Trudy Inst. Fiz. Khim, Akad. Nauk, USSR, 2 Issledovaniya pa Korrozzi Metal., No. 1, 110-25 (1951).

21. "Electrochemical Investigation of Anodic Films on Aluminum," ibid., 126-35.

22. "Some Relations in the Growth of Anodic Oxide Films on Aluminum in Sulfuric Acid," ibid., 136-45.

23. F. Solar, "The Properties of Anodically Produced Oxide Layers on Aluminum and Aluminum Alloys," Mitt. Chem. Forsch Inst. Wirtsch. Osterr. 7, 6-12, 29-37 (1953).

24. R. Bahn, "Refractive Index and Thickness of Thin Layers of Aluminum Oxide Produced by Anodic Deposition," Z. Physik 135, 376-9 (1953).

25. "Distribution of Conductivity within Dielectric Films on Aluminum," J. Electrochem. Soc. 100, 222-6 (1953).

26. Max Schenk, "Patent Literature of Anodic Oxidation of Aluminum," Metalloberflaache, B6, 59-61 (1952).

27. "Patent Literature in the Field of Anodic Oxidation of Aluminum," ibid. 6, B43-6 (1952).

28. "Anodization and Multicoloring of Pure Aluminum," J. Proc. Inst. Chemists (India) 23, 118-34 (1951).

29. S. Wernick, "Surface Treatment of Light Metals. VII, Industrial Anodizing Processes for Aluminum Alloys," Sheet Metal Ind. 28, 947-53 (1951); 29, 843-54 (1952).

30. "Surface Treatment of Light Metals. VI. Anodizing of Aluminum." ibid. 28, 79-87, 373-9, 383 (1951).

31. R. Wittwer, "Oxanal Salt E in the Processing of Aluminum and its Alloys," Ciba Rev. (English Edition), No. 92, 3325, 3329 (1952).

32. "Aluminum and its Anodic Oxidation," Galvanotecnia 2, 175-85, 188-91 (1951).

33. R. C. Spooner, "The Abrasion Resistance of Sulfuric Acid Anodic Films on Aluminum and Aluminum Alloys," Can. J. Technol. 29, 479-91 (1951).

34. C. Sonnino, "Anodic Oxidation of Aluminum and its Alloys," U. S. Patent 2,584,400, February 5, 1952.

35. T. Sharaiske, "Action of Ultrasonic Waves on the Formation of Aluminum Oxide Surfaces," J. Electrochem. Soc. Japan 18, 229 (1950).

36. Giles, et al., "Adsorption at Inorganic Surfaces. Part I. An Investigation into the Mechanism of Adsorption of Organic Compounds by the Anodic Film on Aluminum," J. Chem. Soc., p. 4360 (1954).

37. C. Hanson, "Anodizing and Dyeing of Aluminum and Aluminum Alloys," J. Birmingham Met. Soc. 28, 100-27 (1948).

38. J. Patrie, "The Mechanism of Electrolytic Oxidation and the Formation of Layers of Aluminum Oxide," Rev. Aluminum 26, 397-403 (1949), ibid. 27, 3-7 (1950).

39. J. Trillat, "The Action of Ultrasonics on the Course of Anodic Oxidation," Compt. rend., 237, 1147-8 (1953).

40. V. F. Henley, "Some Aspects of Sulfuric Acid Anodizing to Specification D.T.D. 910C," Bull. Inst. Metal Finishing 5, 65-70 (1955).

41. C. Cohn, "Anodized Coatings on Aluminum," Iron Age 175, No. 21, 91-4, No. 22, 95-8 (1955).

42. S. Wernick, "Metal Finishing Research," Product Finishing (London) 8, No. 3, 65-76 (1955).

43. R. Spooner, "The Anodic Treatment of Aluminum in Sulfuric Acid Solutions," J. Electrochem. Soc. 102, 156-62 (1955).

44. D. Vermilyea, "Space Charges in Anodic Films," Acta Met. 3, No. 1, 106-7 (1955).

45. P. Lacombe, "Anodic Processes in Electrodeposition. The Scientific Basis of Anodic Oxidation Treatments of Aluminum and Its Alooys," Trans. Inst. Met. Finishing, Fourth International Conference, London 31, 1-12 (1954).

46. Herenguel, "Industrial Methods of Brightening and Oxidation of Aluminum and Its Alloys," ibid. 31, 15-23 (1954).

47. R. C. Spooner, "Phosphoric Acid Anodizing of Aluminum and Its Application to Electroplating," ibid. 31, 29-45 (1954).

48. "Anodic Phenomena of Very Pure Aluminum in Organic Acid Baths. I. d-c Electrolysis in Mono-carboxylic Acids."

49. A. W. Brace, "Recent Anodizing Research," Metal Ind. 87, No. 13, 261-64 (1955).

50. S. Wernick, "Surface Treatments and Finishing of Light Metals. Part II. Hard Anodic Coatings," Sheet Metal Ind. 32, No. 337, 345 (1955).

51. Yaeger and Hovorka, "Ultrasonic Waves and Electrochemistry. I. A Survey of the Electrochemical Application of Ultrasonic Waves," J. Acoust. Soc. Amer. 25, 441-55 (1953).

52. P. Aziz, "Radioactive Tracers in the Study of Pitting and Corrosion on Aluminum," J. Electrochem. Soc. 101, 120-3 (1954).

53. A. Ruis, "Influence of Alternating Current on the Oxygen Over Potential and on Anodic Oxidation Processes," Analen Fis. Quim 51, 21-30 (1955).

54. I. V. Krotov, "Theory of Formation of Anode Films on Aluminum," Zhur. Fiz. Khim 28, 1550-4 (1954).

55. S. Tajima, "Anodic Oxidation of Highly Pure Aluminum in Organic Acid Baths III. D-C. Electrolysis in Hydroxy Carboxylic Acids and Maleic Acid." J. Electrochem. Soc. Japan 23, 395-99 (1955).

56. K. Nagase, "Increasing Rate of Voltage and the Relation Between Residual Current and Formation Time on Formation of an Aluminum Oxide Film," Mem. Inst. Sci. Ind. Res., Osaka Univ., 12, 67-81 (1955).

57. U. F. Henley, "Chemical and Anodic Treatments," Light Metals 18, 347-8 (October 1955), 368-9 (November 1955).

58. F. S. Buchler, "Vitreous Enamel Coatings on Light Metals," Metal Ind. 87, 303-5 (October 1955).

59. Ralph Mason, "Factors Affecting the Formation of Anodic Oxide Coatings in Sulfuric Acid Electrolytes," J. Electrochem. Soc. 102, 671-5 (1955).

60. Etienne and Flusin, "Surface Treatment of Aluminum and Its Alloys, I. Mechanical Treatment," Revue del' Aluminum 32, No. 224, 821-30 (1955).

61. P. Shchigolev, "Effect of Electropolishing on the Physicochemical Properties of Pure Aluminum," Fhur. Fiz. Khim. 29, 682-4 (1955).

62. Hunter and Fowls, "Factors Affecting the Formation of Anodic Oxide Coatings," J. Electrochem. Soc. 101, 514-19 (1954).

63. N. D. Pullen, "Continuous Anodic Oxidation of Aluminum Wire," Rev. Met. 52, 731-4 (1955).

64. A. M. Peers, "Non-Uniform Anodic Dissolution. Water-line Attach," Trans. Faraday Soc. 51, 1748-54 (1955).

65. J. F. Dewald, "A Theory of the Kinetics of Formation of Anode Films at High Fields," J. Electrochem. Soc. 102, 1-7 (1955).

66. Hunter and Fowle, "Determination of Barrier Layer Thickness of Anodic Oxide Coatings," J. Electrochem. Soc. 101, 481-5 (1954).

67. Keller, Hunter, and Robinson, "Structural Features of Oxide Coatings on Aluminum," J. Electrochem. Soc. 100, 411-19 (1953).

68. R. C. Spooner and D. P. Seraphim, "Phosphoric Acid Anodizing of Aluminum and Its Application to Electroplating," Trans. Inst. Met. Finishing, Fourth International Conference, London, 31, 29-45 (1954).

69. Hans Burkhardt, "Anodic Brightening and Polishing of Articles of Aluminum on Aluminum Alloys," German Patent 825,937, December 27, 1951; (CA 49, 6752).

70. Frederick H. Hesch, "Anodic Treatment of Aluminum Surfaces," U. S. Patent 2,703,781, March 8, 1955; (CA 49, 6010).

71. I. V. Krotov, "Theory of the Process of Formation of an Anodic Film on Aluminum," Zhur. Fiz. Khim 28, 1550-4 (1954); (CA 49, 5997).

72. Skoulides and Mentoyannis, "Distinction of Two Layers of Aluminum Oxide in Anodically Oxidized Aluminum." Chim Chronika 19, 88-92 (1954); (CA 49, 6060).

73. Walter Kohler, "The Deformability of Anodically Oxidized Pure Aluminum," Werkstoffe U. Korrosion 6, 169-80 (1955); (CA 49, 12994).

74. Mason and Fowle, "Anodic Behavior of Aluminum and Its Alloys in Sulfuric Acid Electrolytes," J. Electrochem. Soc. 101, 53-9 (1954).

75. "Anodic Oxidation of Aluminum and Aluminum Alloys," Swiss Patent 281,448, June 16, 1952, to CIBA, Ltd; (CA 48, 3884) Electrolyte bath additives.

76. H. Bardot, "The Use of Electrical Conductors in Anodizing Aluminum Strip and Wire for Aeronautical Use-Insulating and Refractory Characteristics of Alumina," Congr. Materiaux Resistant A Chaud, A.E.R.A. 1951, 165-9.

77. Zezula and Franklin, "New Aluminum Hard Surfacing Process Gives Hard, Abrasion-Resistant Coating," Western Metals 12, 53-5 (1954).

78. Young and Hain, "Providing Aluminum with a Flexible Oxide Coating," (General Electric Company), U. S. 2,665,243, January 5, 1954; (CA 48, 4418).

79. W. H. Wood, "Anodic Treatment of Aluminum Surfaces," U. S. 2,681,310, June 13, 1954; (CA 48, 10462) - Treatment with hydrophilic colloids.

80. G. L. Deniston, "Producing Black Oxide Films on Aluminum," U. S. 2,681,873, June 22, 1954; (CA 48, 10526).

81. S. Nishikawa, "Anodized Films on Impure Aluminum," Seisan Kenkyu 3, 439-42 (1951); Complete Abstract Japan. Chem. Lit. 26, 68-9 (1952); (CA 48, 12582).

82. A. W. Brace, "Hard Anodizing of Aluminum and Its Alloys," Electroplating and Metal Finishing 7, 329-34 (1954). - a review.

83. Maston Gauthier, "Anodic Oxidation of Aluminum," U. S. 2,685,563, August 3, 1954; (CA 48, 11964). - Addu. of Alkali or Alkaline Earth Halides to H_2SO_4 Baths for a.c. anodizing.

84. H. Willsdorf, "The Growth of Electrolytically Produced Porous Aluminum Oxide Coatings," Zeitschrift fur Angewandate Physik 2, 17-20 (1950).

85. "Anodizing of Aluminum - Recent Advances." Light Metals 18, 91-3 (1955).

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WADC TECHNICAL REPORT 58-13

PART II

HIGH-TEMPERATURE INSULATION FOR WIRE

By

J. N. HARRIS AND J. D. WALTON

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

FEBRUARY 28, 1959

CONTRACT NO. AF 33(616)-3944

WRIGHT AIR DEVELOPMENT CENTER

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Materials Laboratory
Contract No. AF 33(616)-3944
Project No. 7350

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Engineering Experiment Station of the Georgia Institute of Technology under USAF Contract No. AF 33(616)-3944. This contract was initiated under Project No. 7350, "Ceramic and Cermet Materials," Task No. 73500, Ceramic and Cermet Materials Development, and was administered under the direction of the Materials Laboratory WCLT, Wright Air Development Center, with J. J. Krochmal acting as Project Engineer.

This report covers the second year's work, from 1 February 1958 to 31 January 1959. The first year's work was covered in WADC Technical Report 58-13 Part I. Principal personnel participating in this work included J. N. Harris, J. D. Walton, J. W. Johnson and R. C. Mattison.

ABSTRACT

Aluminum coatings plated on substrates of copper, chrome, iron and Inconel were successfully anodized but efforts to anodize aluminum coatings plated over barrier layer metals on copper were unsuccessful.

Since aluminum-clad copper wire has become commercially available, work on aluminum plating of copper wire with barrier layer metals has been stopped.

Two types of sealing coatings for anodized aluminum were considered: (1) frit-resin, (2) colloidal silica.

Proper curing of frit-resin coatings applied to substrates of iron eliminated all reaction with the substrate. Coatings were continuous to the 1300° to 1400° F range but a wetting problem was encountered above 1400° F.

Frit-silicone resin compositions were applied to aluminum wire in two separate coats to eliminate gelling problems encountered when frit and resin were milled together. Electrical properties of frit-silicone and frit-epoxy resin coatings applied to anodized wire were determined.

Colloidal silica was deposited electrophoretically on anodized aluminum as a possible substitute for frit-resin coatings.

Work on a "one time at temperature coating" showed possibilities of continuous operation to 900° F. Work was limited to 1100° F due to the softening of aluminum in this range.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Richard R. Kennedy
Chief, Metals Branch
Materials Laboratory

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INTRODUCTION

The ever increasing speeds developed and anticipated by air and space vehicles are creating higher and higher ambient temperatures. Electrical components operating under these higher temperature conditions are seriously handicapped by the lack of suitable insulating materials.

This report covers the second year's work on a project initiated on February 1, 1957. This project has as its objective the development of wire insulation for application between -85° F and 1500° F. More specifically, the wire should have the following properties:

1. High dielectric strength (400 v/mil and higher)
2. Low loss tangent (.01 and smaller)
3. Low dielectric constant (maximum 4.5)
4. Sufficient flexibility at room temperature to allow the coated wire to be wrapped around a mandrel ten times the diameter of the wire.
5. High impact strength
6. High abrasion resistance
7. Pressure change resistant
8. Thermal shock resistant
9. Corrosion resistant to oils and salty atmosphere
10. Low strategic material content
11. Minimum weight
12. Maximum imperviousness to moisture
13. Maximum reflectivity
14. Concentricity of coating
15. Life expectancy of at least 10,000 hours.

A. Background

The greatest need for flexibility of a wire insulation would be during installation at room temperature. The approach taken by Georgia Tech was to combine an organic and an inorganic coating in the form of a resin with a powdered glass filler, the resin providing the necessary initial flexibility. Once this insulation system is heated up, the resin should burn out and the powdered glass filler should fuse, forming a continuous coating to 1500° F. At 1500° F, however, a vitreous enamel coating would have poor electrical properties unless a stand-off insulator were provided to keep the viscous molten coating from contact with the bare wire. A refractory base coating would provide this stand-off insulator. Several refractory base coatings have been considered; among these were aluminum phosphate and aluminum oxide coatings.

B. Results of First Year's Work

The first year's work on this contract was described in detail in WADC Technical Report 58-13, Part I, "High Temperature Insulation for Wire" by J. D. Walton

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and J. N. Harris. The significant results of the first year's work are as follows.

Work with ceramic-organic combinations as sealers for refractory base coatings indicated that an epoxy resin was best suited for use in these coatings because its burn-out temperature was about the same as that of the silicone resins and its compatability with frits was significantly higher.

Curing studies on frit-resin coatings pointed up the fact that curing was a significant variable and further studies along these lines were needed. The Haveg resin used appeared to have a burn-out temperature high enough to produce a continuous coating with the frit compositions being used. The ceramic coatings did not wet the metal strips properly in the range of 1300° to 1500° F. Frit combinations applied alone (that is, not containing resin) gave a smooth coating in this region. Therefore, it was concluded that the combination of the resin and frit caused the nonwetting in the 1300° to 1500° F range. Curing studies completed in this period showed that cures at higher temperatures and for long periods of time decreased this nonwetting tendency. It was felt that this tendency would be reduced further when the coatings were applied to an aluminum oxide base rather than metal.

Equipment was developed for plating of aluminum on copper substrates from an ethereal solution of lithium aluminum hydride. Coatings of aluminum suitable for anodizing were obtained on copper wire.

The anodized aluminum base coating seemed to hold the most promise as a refractory flexible base coating. The one limiting factor appeared to be the hygroscopic nature of such a coating which in the presence of moisture might cause the dielectric strength to be reduced considerably. The sealing ceramic-organic coating should eliminate this difficulty, however.

SUMMARY

A. Base Coatings

Aluminum oxide was selected for use as a base coating because of its flexibility and its electrical properties. The method decided upon to apply the aluminum oxide coating was to anodize an aluminum coating on copper wire. Application of aluminum to copper wire by electroplating proved feasible; however, the need for a barrier layer metal to prevent solubility of the aluminum in copper caused greater problems as far as anodizing aluminum coatings on copper wire was concerned. Since two commercial manufacturers were working on the problem of cladding copper wire with aluminum, it was decided to obtain commercially clad wire and to concentrate further research efforts on the development of flexible anodized coatings.

Anodizing techniques were worked out using 2 S aluminum wire.

Anodized coatings obtained by the use of phosphoric acid electrolyte proved superior to all other coating techniques investigated. These coatings proved to be very flexible and had good electrical properties. The coatings obtained could

be bent around a mandrel less than ten times the diameter of the wire as required by the contract. Electrical properties of these coatings were also as good as those of sulfuric and oxalic acid electrolytes. A sealing coating is definitely needed for this aluminum oxide coating. When this coating was subjected to the continuity test described in the experimental procedure, vigorous bubbling occurred on the surface of the coating.

B. Sealing Coatings

Frit-resin sealing coatings appear to offer some possibilities. Frit - epoxy resin combinations have thus far given continuous coatings over the range from room temperature to 1500° F when applied on substrates of iron. These coatings have only been tested as sealers for aluminum oxide coatings to 1100° F because of the softening at that temperature of the anodized aluminum wire to which they were applied. The dielectric constants on these wires were high both in the tests made by the University of Illinois and in the screening tests conducted in our laboratory. The dissipation factors varied widely, probably due to pinhole defects in the coatings. All wire coatings made thus far have been on short lengths of wire so the problem in quality control of the thickness of the insulating coating obtained has been great. This problem should be greatly reduced with a continuous operation. Frit - silicone resin compositions gave lower values for dielectric constant and less variation in dissipation factor than did the frit - epoxy resin compositions tested; however, flexibility of the frit - silicone resin compositions was not as good as the flexibility obtained with the frit - epoxy resin compositions.

The best results obtained thus far in sealing anodized coatings has been by the use of colloidal silica. Much lower dielectric constants were obtained with this type of system but again the wide range in dissipation factors suggests that pinhole type defects exist in these coatings. This problem should also be lessened with a continuously operating coating system. Continuity tests made on these wires gave good results. No bubbling was observed on the surface of the colloidal silica-coated wires when 22 volts of direct current were applied to these wires in a sodium chloride solution. In contrast, an anodized wire not impregnated with colloidal silica bubbled vigorously in the sodium chloride solution with only 3 volts potential.

Flexibility of the silica-impregnated wires was good although cracking of the coatings was observed when they were bent around a mandrel 20 times the diameter of the wire; in most cases electrical breakdown did not occur with the first cracking. The cracking of the coating as reported in Table XIII was only on the inside of the bend. In cases where moisture was not a problem, "stand off insulation" would still be achieved since the coating on the outside of the bend remained intact.

A wire coating for one time use (in a missile or rocket) could possibly be achieved by coating an anodized wire with a silicone resin. The resin would provide low temperature protection against moisture. At higher temperatures the resin would burn out but the moisture problem would then be nonexistent. Wires coated with silicone resin have consistently given good results up to temperatures

of 600° F for long periods of time. The flexibility of these coated anodized wires has been very good and the continuity of the coating has been good before and after bending. Tests are now in progress that indicate that the silicone resins may effectively seal the wires to 900° F.

EXPERIMENTAL WORK

A. Base Coatings

1. Aluminum Coatings on Copper Wire

As a result of the first year's work, the best method of obtaining an aluminum oxide coating on copper seemed to be by anodizing an aluminum coating on copper wire.

The 14- to 28-volt motor generator set used with the aluminum-plating equipment described in WADC Technical Report 58-13, Part I, did not have enough versatility to meet the voltage and amperage requirements needed for a complete aluminum-plating study. This power supply was changed to a selenium rectifier bridge capable of delivering 110 volts of direct current at 6 amp with an a-c input voltage of 156. The a-c input is controlled by a variac.

The apparatus for plating aluminum as originally set up used a 2 S 1/2-inch aluminum rod as the anode which could be adjusted in order to vary current and voltage. Difficulty was encountered in obtaining uniform coatings on both sides of the copper plates. Wire coatings were fairly concentric about any point on the wire but varied considerably in thickness along the length of the wire. Replacing the 1/2-inch rod by four 2 S aluminum strips equally spaced about the perimeter of the plating bath and extending to the bottom of the plating bath considerably improved the concentricity of the coating about any point on the wire and the uniformity of the coatings over the lengths of the wire. The operation was further improved by replacing the aluminum strips with a plating container made from a 3 S aluminum tube.

To obtain better plating, as recommended by Connor and Brenner,[1] a cam recycling timer was connected to a double pole double throw relay to automatically reverse the polarity of the plating system for any specified interval of time. A 60-minute timer was incorporated into the control panel to measure total plating time. (See Figure 1.) A diagram of the plating circuit is shown in Figure 2. The best plating was obtained on copper wires at a current density of 3 to 4.5 amp/dm^2 with current cycles of 1 to 3 minutes and for times of 1 to 20 minutes. The current was reversed for 10 per cent of each cycle with a total plating time of 10 minutes. The plating bath used in all cases was an ethereal

[1] J. H. Connor and Abner Brenner, "Electrodeposition of Metals from Organic Solutions," Part II, "Further Studies on the Electrodeposition of Aluminum from a Hydride Bath," J. Electrochem. Soc. 103, 657-662 (1956).

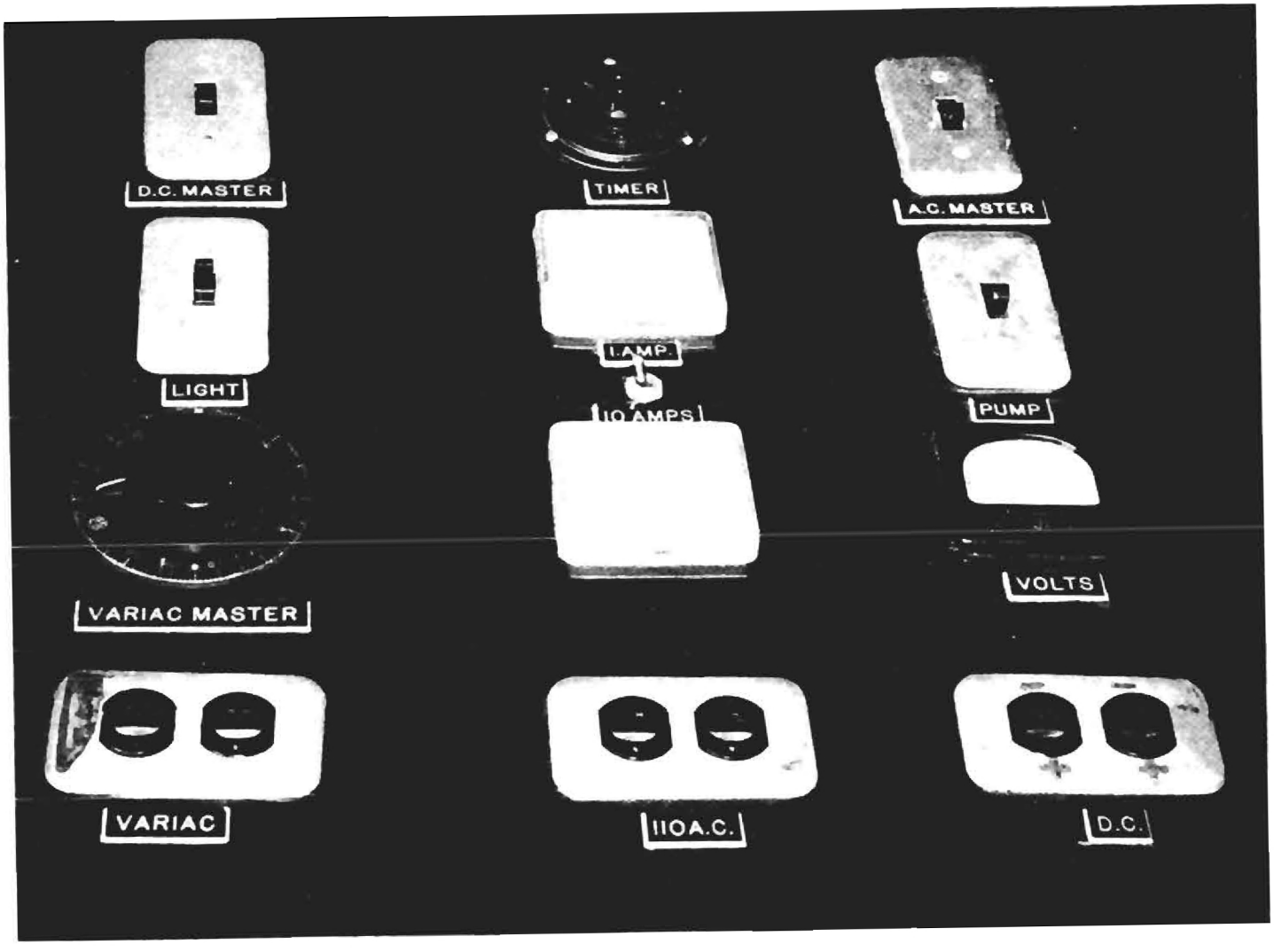

Figure 1. Control Panel for Aluminum-Plating Operation.

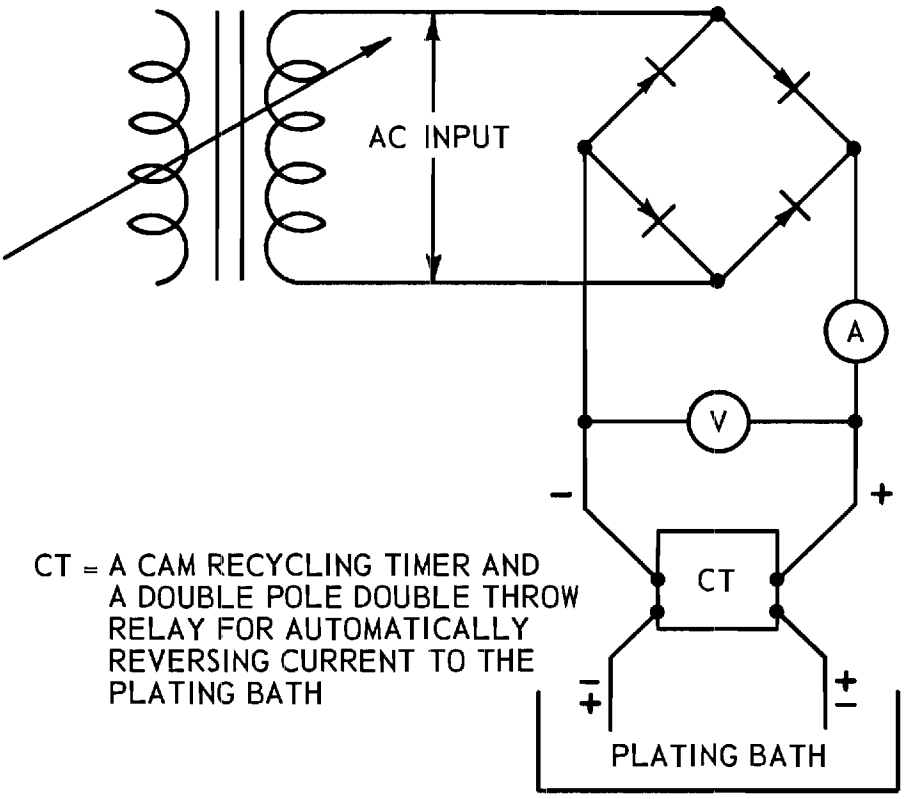

Figure 2. Diagram of Plating Circuit.

solution of 3-molar aluminum chloride and 0.4-molar lithium aluminum hydride. All solutions were made up in the dry box from reagent grade chemicals. Figure 3 is a photomicrograph of aluminum-plated copper wire showing concentricity of the aluminum coating. This particular coating was obtained by the use of a current density of 4.5 amp/dm^2, a current cycle of 3 minutes with the current reversed for 10 per cent of each cycle and a plating time of 10 minutes.

2. Barrier Layers

Upon heating the aluminum-coated copper wire to 1000° F, a large part of the aluminum coating formed a solid solution with the copper. Upon cooling to room temperature the remaining aluminum coating cracked off the copper-aluminum alloy. Smith and Palmer[2] (see Figure 4) have shown that as little as 2 per cent aluminum reduces the conductivity of copper to only 25 per cent of its pure value--58 mho(meter, mm^2). It was decided that a barrier layer would be necessary to prevent the diffusion of the aluminum into the copper.

In selecting promising materials that might be suitable as a barrier layer, it was thought that a metal with a body-centered cubic structure should be used since aluminum and copper have face-centered cubic structures and metals with the same crystal structure tend to be more soluble in each other than metals with different crystal structures. On this basis iron and chromium were selected for plating onto the copper prior to the aluminum plating. Inconel-clad copper wire recently developed by the General Electric Company was available and samples of the wire were on hand. For this reason, Inconel-clad copper wire was included in the study of suitable materials for barrier layers.

Aluminum-plated copper wires were affected by corrosive action due to moisture in normal laboratory air. Wires with a barrier layer of iron between the aluminum and the copper were left side by side with aluminum-plated copper wires on a laboratory bench for a period of several days. In each case, the aluminum coating was approximately 0.3 mils in thickness. The wires with the barrier layer did not show any corrosion, while the wires without the barrier layer corroded severely. (See Figure 5.) Aluminum-plated copper wires left in a desiccator with a drying agent did not corrode.

a. Iron Substrates. Aluminum was plated on iron wires at a current density of 4.5 amp/dm^2 for 20 minutes using a current cycle of 3 minutes and reversing the current for 10 per cent of each cycle. (See Figure 6.)

Aluminum coatings obtained on iron had especially good adherence. It was possible to bend the iron-coated wire around a mandrel of less than ten times the diameter of the wire. These coatings were placed in a furnace at 1000° F for an hour and then removed and allowed to cool in air to room temperature. There

[2] C. S. Smith and E. W. Palmer, "Thermal and Electrical Conductivity of Copper Alloys," Trans. Amer. Inst. Min. Met. Eng., 117, 225(1935).

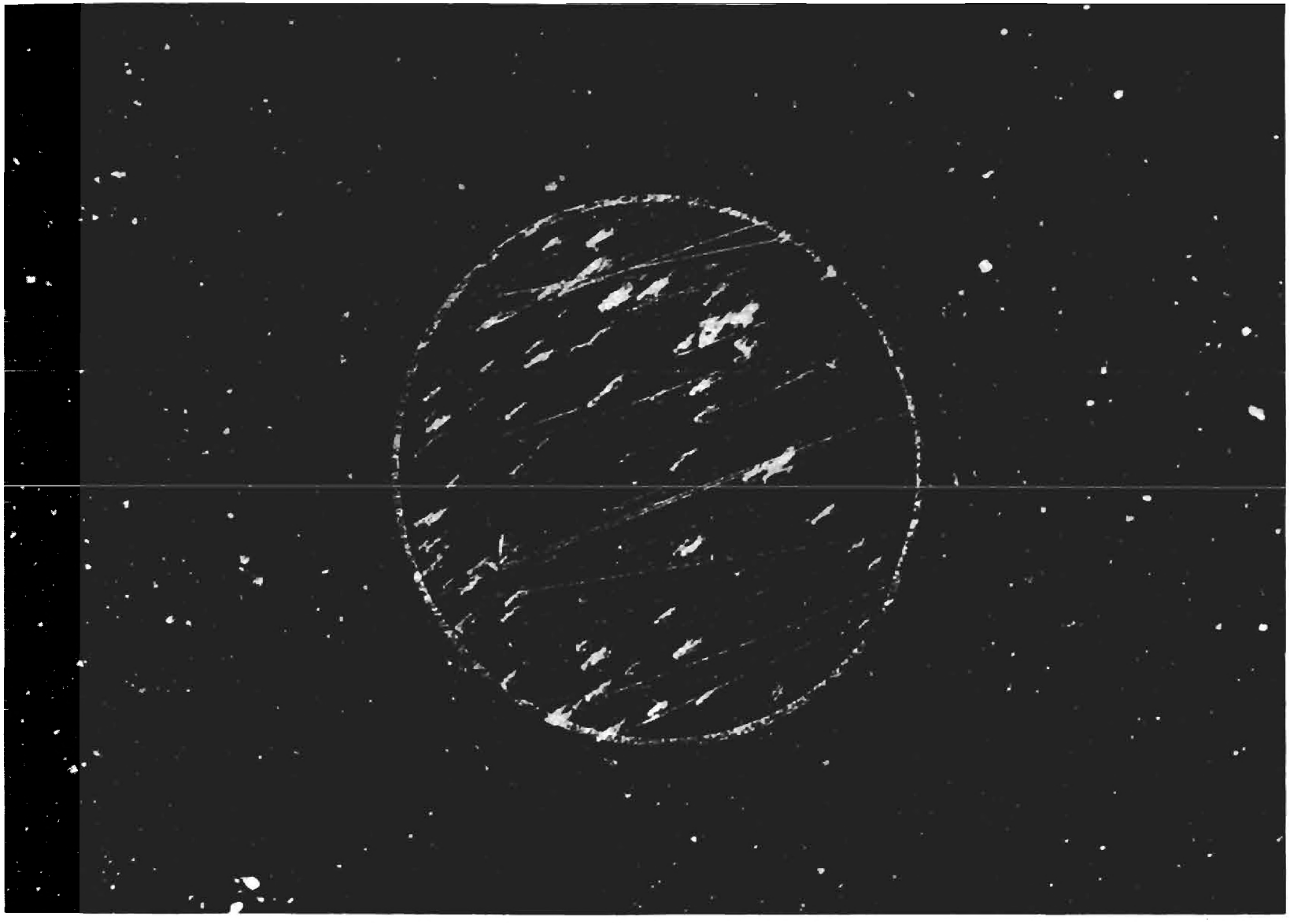

Figure 3. Photomicrograph of Aluminum on Copper Wire. (50x).

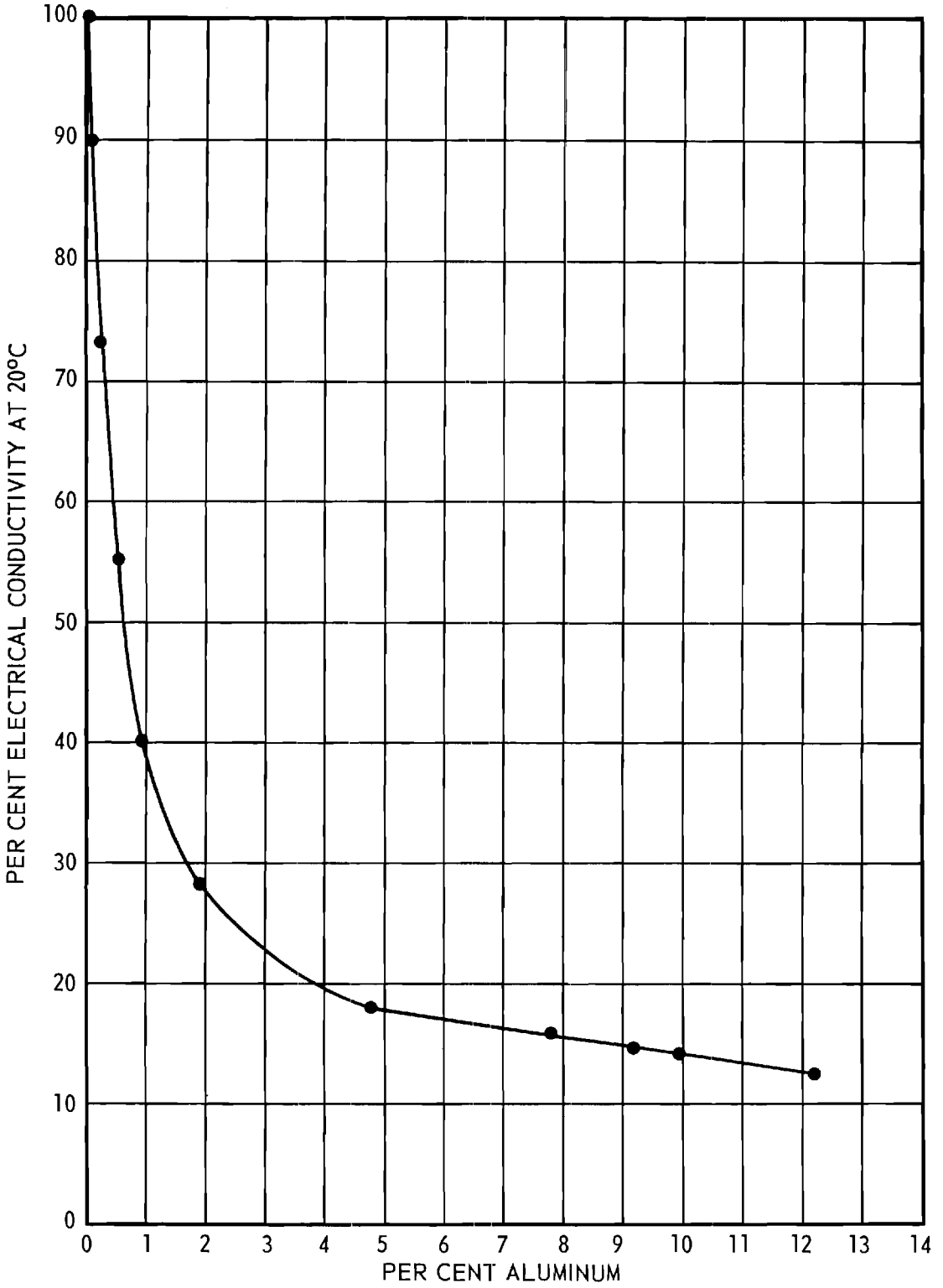

Figure 4. Per Cent Electrical Conductivity of Aluminum-Copper Alloys.

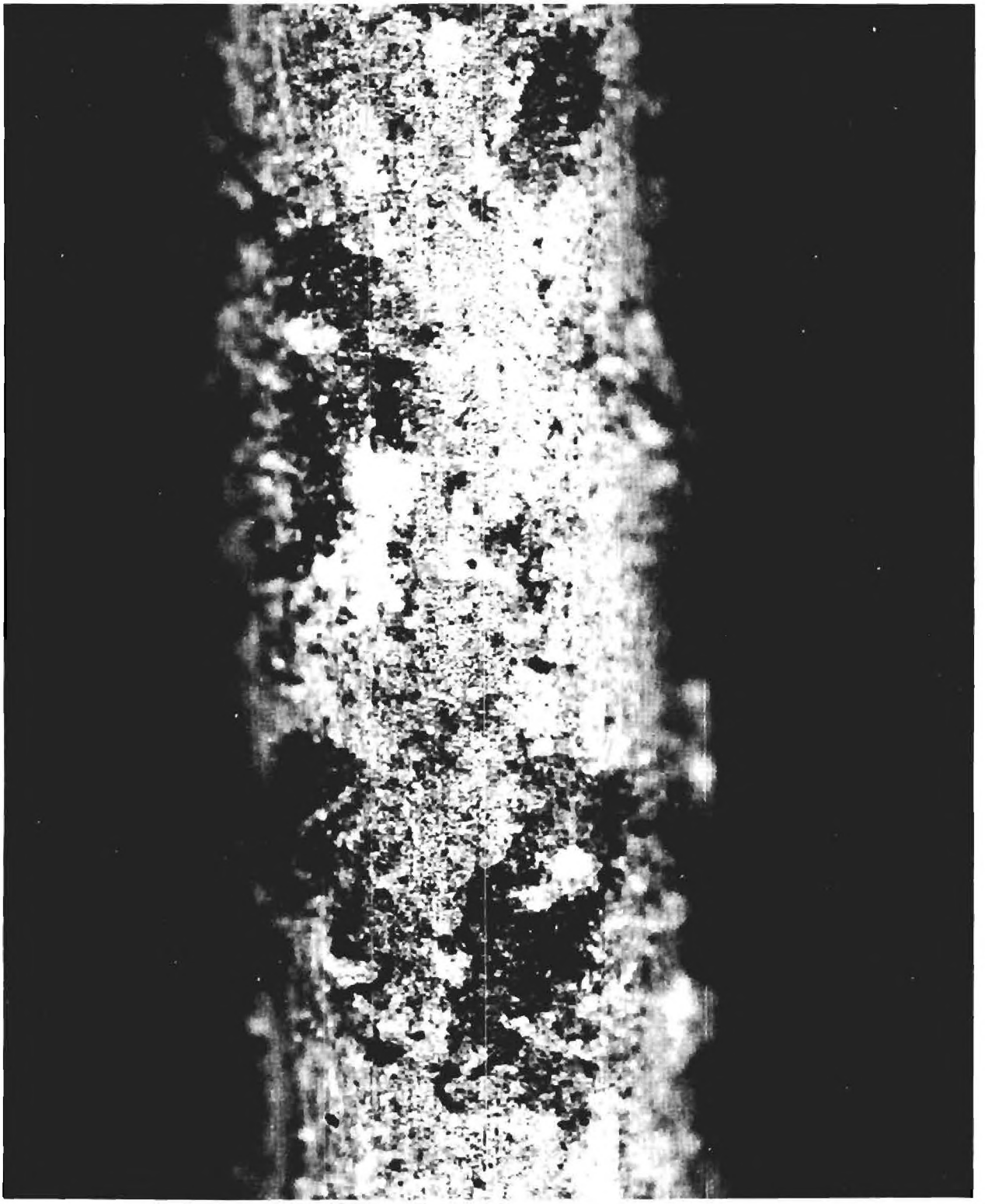

Figure 5. Aluminum-Plated Copper Wire Showing Effects of Corrosion.

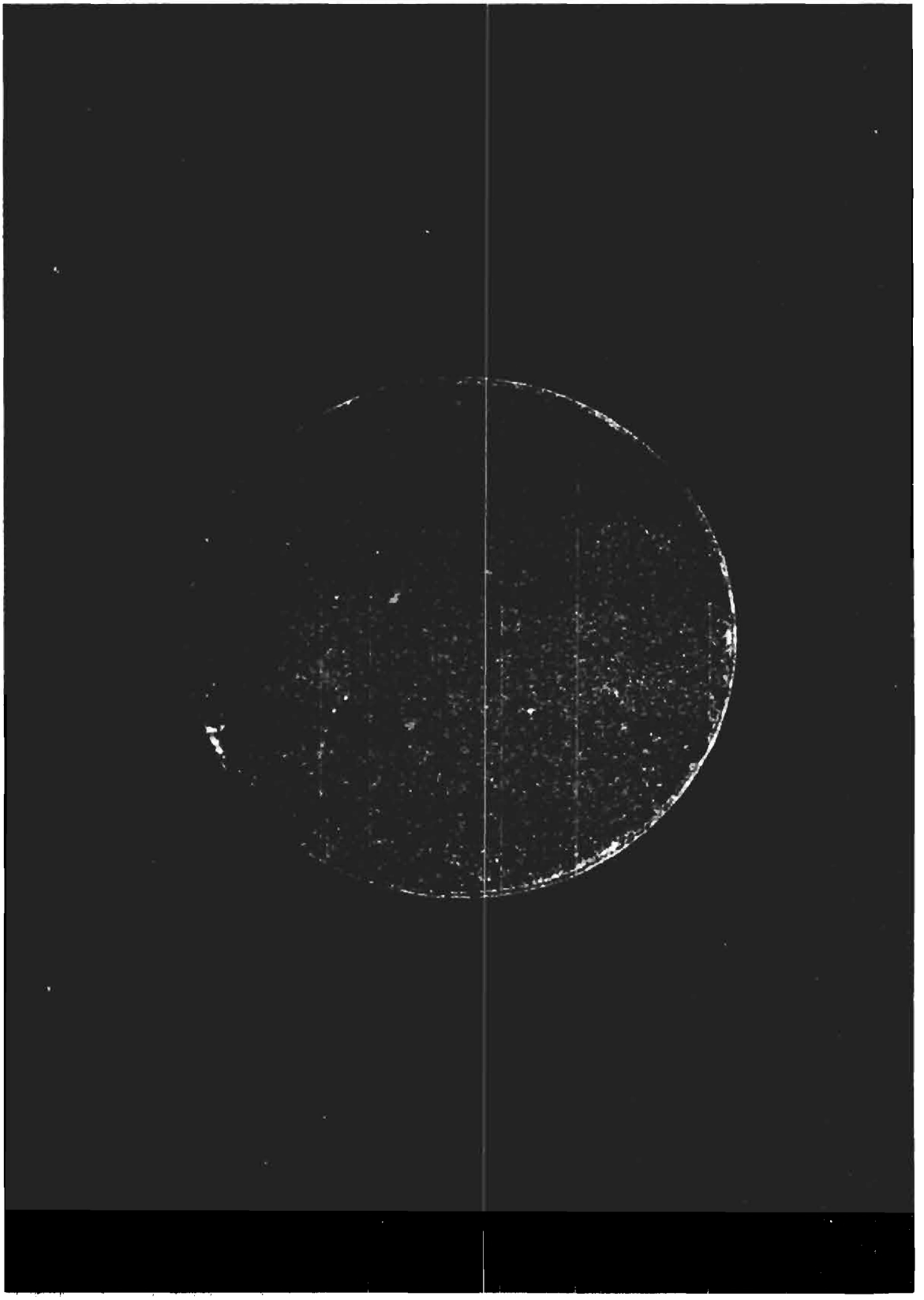

Figure 6. Photomicrograph of Aluminum on Iron Wire. (50x).

was no apparent interaction of the metals and no cracking of the aluminum coating upon cooling.

Aluminum plating on iron wire produced coatings superior to those on copper, so it was felt that iron might be a good barrier layer material and at the same time provide good adherence for the aluminum.

The following iron-plating bath was used:

ferrous chloride ($FeCl_2 \cdot 4H_2O$)	40 oz/gal
calcium chloride ($CaCl_2$)	45 oz/gal.

The bath was operated at 195° F and a current density of 60 amp/ft^2 was used for plating the copper wires as recommended in the Electroplating Engineering Handbook.[3] This current density produced coatings several mils in thickness in short periods of time (1 to 2 minutes). Also the coating would flake off when the coated wires were heated to 1500° F. The current density was reduced to 40 amp/ft^2 and wires plated for 5 minutes; results were erratic in that the coatings showed several shades of color after plating and exhibited poor adherence when the wires were heated. Coatings produced were several mils in thickness.

A study (Table I) of time versus plating thickness was carried out at a current density of 18.7 amp/ft^2. This lower current density was used to achieve thinner iron coatings of one-tenth to two-tenths mils in thickness with longer plating times of 1 to 12 minutes. Thickness of iron plated was measured by weighing the coating. This study was conducted in order to determine (1) the rate of deposition of iron and (2) the degree of roughness of coating with respect to time. The smoothness of the coating increased until a maximum was reached at 12 minutes. In plating copper wires with iron, the most important consideration was thorough cleaning of the copper prior to iron plating. Iron was plated onto copper wire after cleaning using the cleaning procedure of Connor and Brenner.[4] In some instances iron-plated wires had a black matte appearance. Any attempt to brighten this coating by cleaning in acid caused it to be stripped from the wire. The black matte coating is believed to be caused by improper cleaning of the substrate. The adherence of iron to copper could be markedly improved by heating to 1500° F for one hour in an atmosphere of argon. Wire thus treated could be bent very sharply without breaking the iron coating.

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[3] A. K. Graham, Electroplating Engineering Handbook. (New York, Reinhold Publishing Company, 1955) page 208.

[4] J. H. Connor and Abner Brenner, "Electrodeposition of Metals from Organic Solutions," Part II, "Further Studies on the Electrodeposition of Aluminum from a Hydride Bath," J. Electrochem. Soc., 103, 657-662 (1956).

TABLE I

TIME OF PLATING VERSUS THICKNESS OF COATING FOR IRON PLATE ON COPPER WIRE

Time of Plating (Min)	Weight Before Plating (Gm)	Weight After Plating (Gm)	Weight of Coating (Gm)	Length of Wire (Inches)	Thickness of Coating x 10^{-2} Inches
2	4.2140	4.2140	[Control sample, no change due to time in electrolyte]		
2	4.1740	4.1835	0.0095	4.9	0.49
2	4.2140	4.2225	0.0085	4.9	0.44
4	4.1832	4.1962	0.0130	4.9	0.67
4	4.1607	4.1713	0.0106	4.9	0.55
6	4.1730	4.1880	0.0150	4.9	0.77
6	4.0836	4.0973	0.0137	4.9	0.71
8	4.1588	4.1788	0.0200	4.9	1.09
8	4.0856	4.1045	0.0189	4.9	0.97
12	4.1930	4.2220	0.0290	4.8	1.54
12	4.2475	4.2770	0.0295	4.8	1.58

Aluminum plating of iron-coated copper was very dependent on the cleanliness of the iron prior to plating. The ability to plate aluminum on the iron substrate depended on the quality and condition of the plated iron. A shiny metallic iron could be plated with aluminum with no further cleaning. If some time elapsed between the iron-plating and the aluminum-plating operation, or if the wires were heat treated in argon before completing the aluminum-plating operation, the iron-plated wires could be effectively cleaned in 30 per cent (by volume) hydrochloric acid.

b. Chrome Substrates. Chrome plating was applied to copper wire by two processes: (1) a common commercial process and (2) a proprietary process of the Metal and Thermit Corporation (Unichrome CF-500 crack-free compound). Coatings produced by the common commercial process did not have sufficient adherence at elevated temperatures. The Metal and Thermit process produced very good coatings that did not crack on bending around a mandrel less than three times the diameter of the wire upon heating to 1500° F (see Figure 7).

The chrome coating was cleaned in 30 per cent (by volume) hydrochloric acid prior to aluminum plating. The aluminum-plating operation failed to produce a

continuous coating on the cleaned chrome. Bits of chrome metal were visible through the aluminum.

c. Inconel Substrates. Inconel-clad copper wire was cleaned by the method used by Conner and Brenner for cleaning of steel, that is, (a) anodic etch in sulfuric acid (about 74 per cent by volume) current density of 20 amp/dm^2 for 2 minutes, (b) rinse and dry, (c) 10-15 minutes in Quilon diluted 50 per cent with ethyl ether, (d) transfer quickly to bath and plate. Wires cleaned in this manner and plated with aluminum had very poor adherence of aluminum to the Inconel coating. Wires were next cleaned with 30 per cent nitric acid. These wires were plated and again the aluminum had very poor adherence on the Inconel coating. Inconel-clad wires were next cleaned in aqua regia. The aqua regia etched the Inconel coating with the result that the aluminum coating plated on the Inconel had a very rough texture. Attempts to anodize the cleaned aluminum coating were unsatisfactory.

d. Evaluation of Cleaning Procedures. Attempts to plate chromium and iron on copper substrates have shown that cleaning is the most important step in plating.

The cleaning procedure for copper as used by Connor and Brenner[5] has given the most consistent plating results; however, this solution etches the copper badly and causes the plating to be rough. Samples cleaned by other methods have much smoother coatings but are not consistent from sample to sample in that some samples have pits in the coating. A study of cleaning methods for copper prior to plating was initiated; the results are tabulated in Table II.

3. Aluminum-Clad Copper Wire

At least two commercial manufacturers are now working on the problem of cladding copper wire with aluminum. As satisfactory aluminum-clad copper wire became commercially available, work on the aluminum plating of copper wire at Georgia Tech was stopped. Samples of aluminum-clad wire were received from Westinghouse and these samples were successfully anodized. This aluminum-clad wire, with a barrier layer of silver, was ordered in quantities large enough to allow work with continuous lengths of wire. According to Carlson, the silver is used to act as a barrier layer between the aluminum and the copper to prevent the rapid mutual diffusion which they normally undergo at slightly elevated temperatures.[6] The equipment for anodizing and sealing of wire was modified to allow continuous operation.

4. Anodizing

Initially a number of anodizing baths were tried. These included boric acid, chromic acid, oxalic acid and others. From these the sulfuric acid process was selected because of its simplicity of operation and because of the porous coating produced by this process. In the initial tests a 15-per-cent solution of sulfuric acid was used with about 18 volts potential.

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[5] Connor and Brenner, loc. cit.

[6] C. L. Carlson, "Development of Aluminum-Clad Copper Wire," Wire and Wire Products, 770-774 (July 1958).

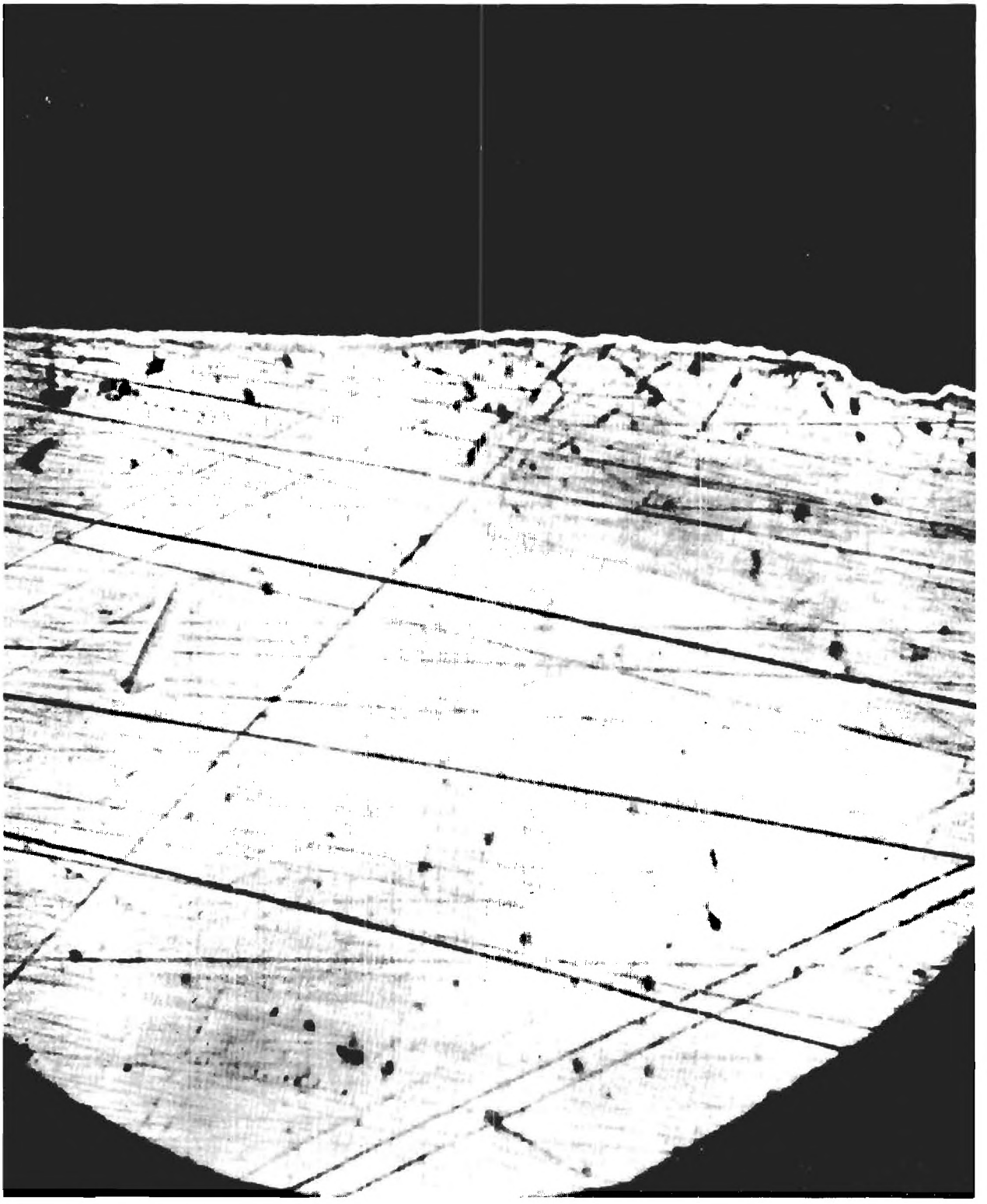

Figure 7. Photomicrograph of Unichrome CF-500 Plate. (1320x).

TABLE II

CHEMICAL CLEANING PROCEDURES FOR COPPER

Substrate	Method of Cleaning	Remarks
Copper	Connor and Brenner[7]	Most consistent plating but samples were badly etched
Copper	Nitric acid, 30 per cent by volume	Only slight etching, plating smoother but not consistent, that is, some wires plated well, others had pin holes.
Copper	Hydrochloric acid, 30 per cent by volume	Same as nitric acid
Copper	Sodium hydroxide, followed by nitric acid, 30 per cent by volume	Second best to Connor and Brenner method

Copper wires coated with a 0.3-mil aluminum coating without any barrier layer metal were placed in a container with the anodizing solution. These wires acted as the anode while four lead strips equidistant around the jar acted as the cathode. Using a variable d-c source, the voltage was slowly raised from 0 to 18 over a period of 2 minutes and these conditions allowed to remain constant for about 15 minutes. The bath was agitated continuously.

It was found that the addition of 2 to 4 per cent glycerine to the bath resulted in an improved coating. A softer, more porous, more flexible film was obtained by use of lower voltages (6 to 8 volts), more concentrated acid solution and a higher bath temperature. However, no coatings were obtained with enough flexibility to meet the terms of the contract. Flexibility was measured by bending the wire slowly around a stepwise mandrel and observing the coating under a 10-power binocular microscope for cracking. Electroplated aluminum coatings on copper wire were anodized easily with this technique; the only problem encountered was in taking care to stop the process at the point where most of the aluminum was oxidized. This was necessary since the aluminum coating was not perfectly concentric and did not maintain the same thickness over the entire length of wire. Equipment consisting of a lead-lined tank and a power supply was constructed for anodizing wire lengths up to 16 inches long. Power was supplied by a bridge selenium rectifier of 6-amp capacity and 120-volt direct current, with 156-volt alternating current input. (See Figure 8.)

[7] Connor and Brenner, loc. cit.

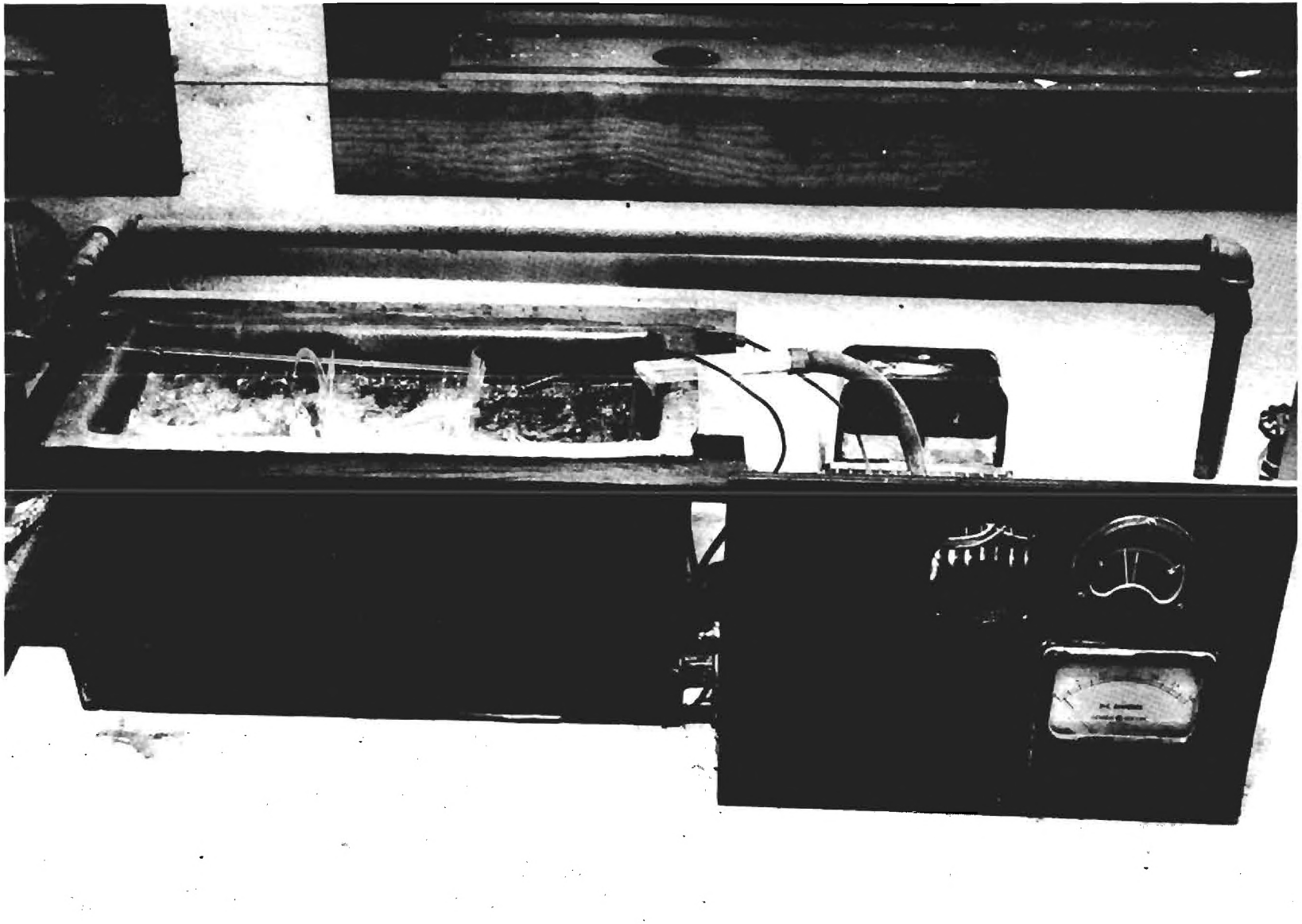

Figure 8. Apparatus for Anodizing in Sulfuric and Oxalic Acid Electrolytes.

Investigations were carried out on 2 S aluminum wire, since aluminum-clad wire with a barrier layer of silver had been ordered but not received from Westinghouse, to determine the characteristics of variations in current density, electrolyte temperature and time of anodizing. Incorporating a sulfuric acid electrolyte of 165 grams of sulfuric acid per liter of water with 2 per cent glycerine, the anodized wires gave hard, adherent coatings which could not be removed with mechanical scraping. Current densities were varied from 8 amp/ft^2 to 20 amp/ft^2 at constant temperature. These wires could be bent around a mandrel less than ten times the diameter of the wire without crazing. Lower current densities gave improved flexibility; however, there was no sharp improvement as the current density was lowered to 8 amp/ft^2. Temperature was increased by 10° increments from 25° C to 65° C at a current density of 8 amp/ft^2. A slight improvement was noted in the flexibility of wires anodized at higher temperatures.

Oxalic acid electrolyte was prepared using 50 grams of oxalic acid per liter of water and adding glycerine to a concentration of 2 per cent by weight. A d-c current was used. Temperature, current density and time of anodizing variations showed the same characteristics as did sulfuric acid anodizing. Using an a-c oxalic acid process, increased flexibility was obtained to current densities of 50 amp/ft^2; however, the coating was so soft that it could be scraped away from the surface of the wire with the fingernail. At lower current densities the a-c process showed little improvement in flexibility with respect to d-c sulfuric and oxalic acid processes.

The best coatings thus far obtained were prepared by the use of 4 per cent (by weight) phosphoric acid solution with 1 to 3 per cent glycerine as an additive. Results showed much improvement over wires previously anodized with oxalic and sulfuric acid electrolytes in that the flexibility of the phosphoric coatings was such that the wires could be bent around a mandrel three times the diameter of the wires without visible spalling or crazing when observed under a 10-power binocular microscope.

The dielectric strength of phosphoric acid anodized wires was measured by ASTM testing methods and found comparable to those of sulfuric and oxalic acid anodized wires.† Only single wires 13 to 16 inches long were anodized. The wire being anodized was rotated rapidly in the electrolyte by a small laboratory stirrer motor. The time of anodizing was 25 to 30 minutes. (See Figure 9.) The optimum operating temperature was 40° to 55° C; higher temperatures tended to etch the wires chemically. Current densities varied from 120 to 250 amp/ft^2. More important than the current density was the amount of current passed; the quantity being roughly proportional to thickness when rate of solution of coating approximated coating deposited. The nature of the electrolyte required that voltages be increased gradually from 0 to 125 volts to maintain a constant current density. Rapid application of potential to a piece caused breakdown of the aluminum oxide layer with subsequent surge of current through that spot. Such wires corroded rapidly at the point of rupture, acting similarly to a dead short. In addition, operating above 250 amp/ft^2 or failure to maintain sufficient agitation of either the anode or the electrolyte caused rupture of the barrier layer.

†ASTM STDS B-110-45.

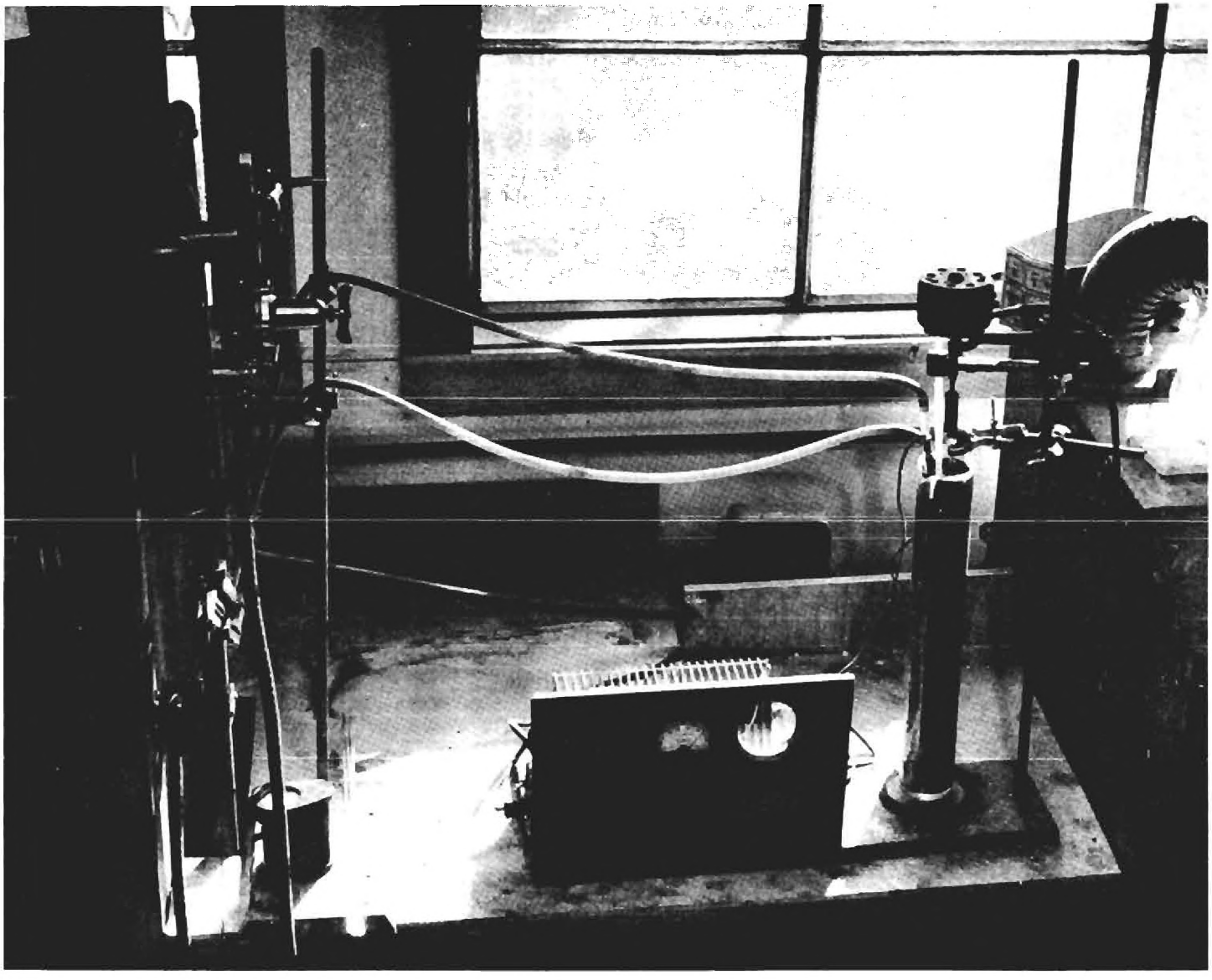

Figure 9. Equipment for Phosphoric Acid Anodizing of Single Wires.

The anodizing equipment was modified for producing continuous lengths of phosphoric-anodized wire. The modified apparatus consists of the previously constructed anodizing tank to which has been added a rack which permits the wire to make several passes through the electrolyte so that approximately 6-1/2 feet of the wire are in the electrolyte while anodizing is in progress. A take-up spool driven by a synchronous motor and a gear arrangement pulls the wire through the bath at a rate of 2.9 inches per second. This gives the wire a total time in the anodizing bath of 27 minutes.

TABLE III

FRIT-RESIN COMBINATIONS USED IN CURING STUDIES

Composition	A	X	Y	Z
Haveg Resin Non-Aromat No. 6 (Ml)	130	150	130	130
Acetone (Ml)	20	15	20	20
Frit No. 231 (Gm)	50	---	85	95
Frit No. 263 (Gm)	25	95	10	5
Frit No. 3E46R (Gm)	25	---	---	---
Frit No. XG-201 (Gm)	---	5	5	---

B. Sealing Coatings

To prevent dielectric breakdown of aluminum oxide coatings at low temperatures resulting from penetration of moisture to the base metal through the pores of the aluminum oxide, a sealing coating is needed.

1. Ceramic-Organic Coatings

Investigations of frit-resin coatings begun the first year have been continued. Main efforts were placed on curing studies of frit-resin combinations developed during the first year. These combinations are shown in Table III above.

Curing studies were run on each of the frit-resin combinations by spraying coatings on 12-inch iron strips and curing at temperatures of 200°, 400° and 450° F without curing agent (Table IV). In this study a problem arose. A yellow bubbly area full of blisters and pinholes appeared between 1250° F and 1400° F in almost all tests. Possible sources of this trouble area were thought to be (1) materials in the dryer being dried simultaneously with the curing studies, (2) a component in one or more of the frits or resin, (3) colloidal carbon left behind during burn-out of the resin, or (4) a reaction between the constituents of the frit-resin-iron system.

The frit-resin coatings were first isolated in a dryer so that no other vapors were present in the dryer atmosphere other than those in the frit-resin-iron system. This failed to eliminate the yellow color on curing and firing.

Each of the frit components were investigated by combining single frits with the resin, applying to enameling iron and curing the coatings. The yellow color was still present.

TABLE IV

CURING STUDIES ON FRIT-RESIN COMBINATIONS

Trial No.	Coating	Temp. (° F)	Time (Hr)	Remarks
1 - 1	A	200	15	Resin burn-out (800° to 1000° F) Yellow bubbly area (1300° to 1500° F)
1 - 2	A	200	24	Resin burn-out (800° to 1000° F) Yellow bubbly area (1300° to 1500° F)
1 - 3	A	200	36	Shorter resin burn-out region Yellow bubbly area (1300° to 1500° F)
1 - 5	A	450	2	Marked decrease in resin burn-out Yellow area (1300° to 1500° F)
1 - 6	A	450	3	Same as 1 - 5
1 - 7	A	450	4	Same as 1 - 5
1 - 9	A	400	4	No resin burn-out Yellow area still present
1 - 10	X	400	2	Resin burn-out; yellow area
1 - 11	Y,Z	450	1	Both coatings continuous to 1250° F No yellow area
1 - 12	Y,Z	450	2	Resin burn-out (750° to 1000° F)
1 - 13	Y,Z	450	3	Coatings continuous to 1400° F No yellow color
1 - 14	Y,Z	450	4	Z burn-out of resin (750° to 1000° F) No yellow color Y had raised yellow area

Since most frit-resin combinations exhibited the yellow area it was thought that the carbon from the resin might be causing it. A frit-resin-coated strip was fired in an atmosphere of argon so that the carbon would not oxidize. After firing, the strip was not evenly coated since the carbon residue kept the enamel from wetting the metal.

Burning organic matter might be responsible for a reducing atmosphere in the bottom of the gradient furnace, causing the carbon to oxidize incompletely. A suspension of colloidal carbon might cause the yellow color. A tube was inserted in the gradient furnace and a low flow of air allowed to pass through the furnace while firing frit-resin-coated strips. This did not eliminate the yellow color but tended to reduce it.

Mill additions of ammonium meta vanadate and of sodium nitrate were added to mill batches of frit-resin combinations to act as oxidizers; but upon curing and firing the yellow area was still present.

A new gradient furnace was constructed open on both ends so that a continuous flow of air would pass across the specimen while firing. This furnace was so constructed that the hot zone (1500° F) is at the top and the cool zone (400° F) at the bottom. It was built by winding resistance wire around a 1-1/2-inch-diameter aluminum oxide tube. The tube is supported in a 12-inch diameter shell and is insulated by light magnesium oxide. The furnace is equipped with 11 thermocouples for measuring the temperature with a portable potentiometer. A porcelain cap containing numerous small holes reduces the flow of air through the furnace. The specimen to be fired is supported by a hook attached to the porcelain cap (see Figure 10). Firing of frit-resin-coated strips reduced the yellow area but a large part was still present.

The combination of the frit-resin-iron system was then studied as a possible source of the yellow-colored bubbly area. Stainless steel, Inconel and copper substrates were sprayed with several frit-resin combinations. Anodized aluminum-coated copper strips were also sprayed with frit-resin combinations. All coatings flaked off the copper upon cooling, but on the stainless steel and Inconel the coatings remained in fair condition. No yellow color or bubbly area were found in these coatings. The coatings applied to the anodized aluminum tended to take the aluminum oxide into solution, leaving a cracked coating on the copper.

Further study on the proper curing of the frit-resin coatings showed that the yellow color could be eliminated when the frit-resin coatings were fired on iron. The optimum cure for Coatings A, X, Y and Z was found to be at 400° F for a period of 24 to 36 hours. Smooth continuous coatings to 1400° F were obtained; above this temperature the enamel glass failed to completely wet the surface of the enameling iron.

A curing study was initiated to determine if better coatings could be obtained by using a cold curing agent. Table V shows the results of this study.

Doubling the amount of curing agent per pound of resin and allowing the coating to cure for 24 hours at 220° F eliminated the yellow color and bubbly area but the resin burned out before fusion of the frit.

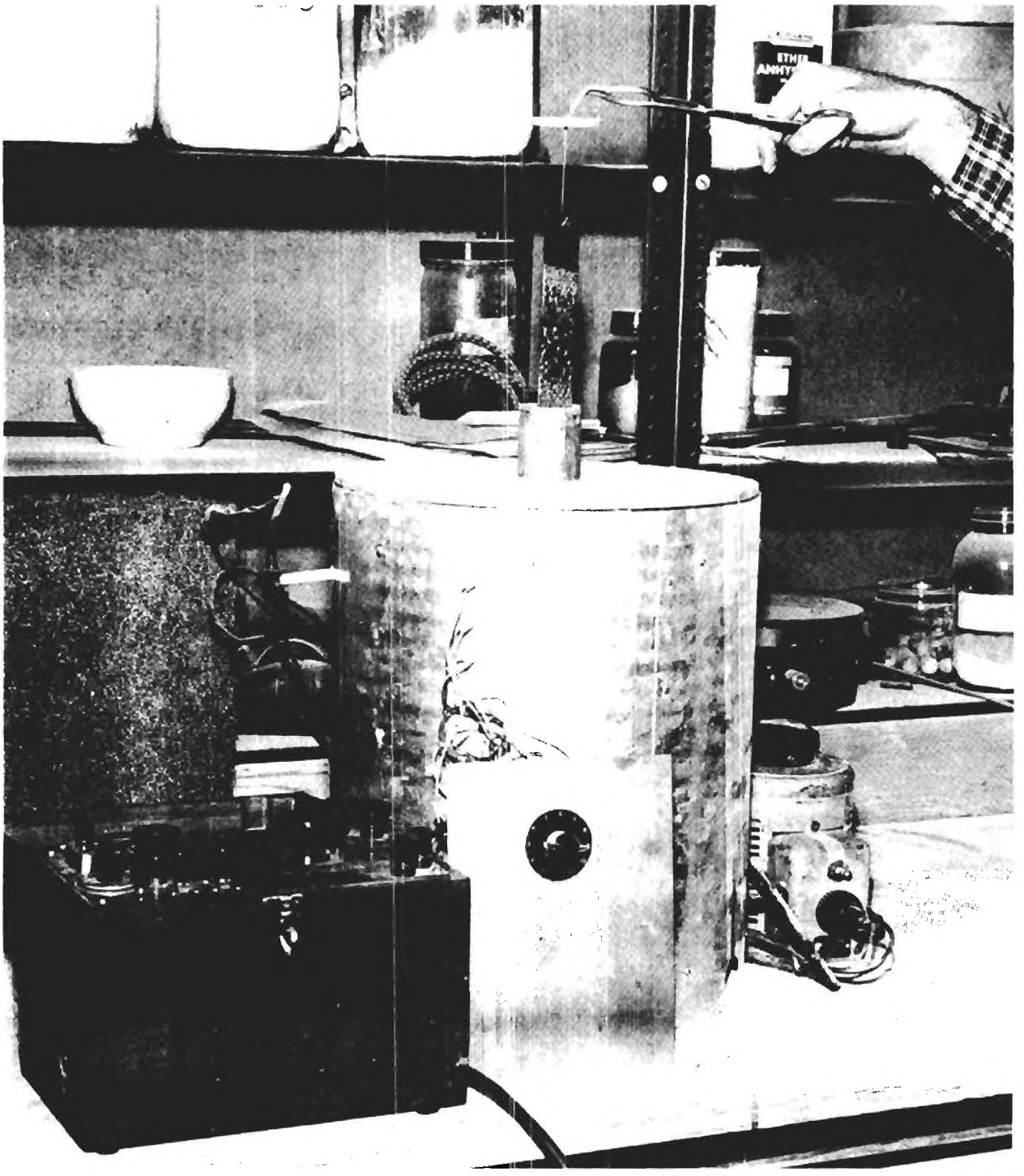

Figure 10. Method of Firing Sample in Gradient Furnace.

The results of these studies led to the conclusion that heat curing was the best method.

2. Ceramic-Organic Coatings Applied to Anodized Wire

Frit-resin coatings were applied to anodized aluminum-coated iron strips. The iron strips were Armco low carbon enameling iron plated with aluminum in our laboratory. After curing, the frit-resin coated strips were fired to 1500° F. A smooth glassy coating was obtained in the center of the strip but along the edges the coating was too thick and blistering was encountered. None of the yellow color previously associated with the frit-resin coatings when fired on iron strips was encountered.

TABLE V

CURING STUDIES USING HAVEG CURING AGENT NO. 6†

Trial No.	Coating	Temp. (° F)	Time (Hr)	Remarks
3 - 1	A - X	70	24	Yellow area, chipping 1200° F
3 - 2	Z - Y	70	20	Yellow area, excessive bubbling
3 - 3	A-Z-Y	70	40	Yellow area, cracking

† 3.22 ml of curing agent per pound of resin added to each composition.

A number of 2 S aluminum wires were anodized in an effort to study the low temperature characteristics of frit-resin coatings when applied to anodized wire surfaces. Frit-resin coatings were applied to anodized aluminum wire by two methods. The first method is the same as that used previously, that is, a frit-resin combination was applied as a single coating. The second method was to apply the frit and resin separately in two coats. The frits were milled with water and the resulting slip applied to the anodized aluminum wire by dipping. After the coating of frit dried, resin was applied by dipping, allowed to dry and the composite coating cured. Coatings applied by both methods appear to have equal flexibility at room temperature. Frit-resin Composition Y was applied to the wires by dipping. The coating was air dried for 24 hours to allow evaporation of volatile components and cured by heating to 400° F for 4 hours. After curing, the coating would take very little bending without cracking. A modified Composition Y was prepared using 170 ml of acetone rather than 20 ml. This coating was then applied to anodized aluminum wires, air dried and cured as above. This thinner coating had somewhat more flexibility but still was unsatisfactory. Anodized aluminum wires with Frit-Resin-Coating Y have been heated to temperatures just below the melting point of the aluminum wires. A smooth coating was obtained at all temperatures but the coating had very little abrasion resistance in the 600° to 900° F range.

Room temperature flexibility and continuity of frit-resin coatings made with Non-Aromat Resin No. 6 were markedly improved by substituting allyl glycidyl

ether for the acetone previously used. Good flexibility was obtained with the frit-resin coatings; however, flexibility varied greatly with thickness of the coating. Coating short lengths of wire presented a problem in quality control of coating thickness. This problem should be lessened with a continuous operation.

The ability to apply frit and resin separately and still obtain adherence and flexibility warranted a re-evaluation of silicone resins because of their higher burn-out temperatures and superior electrical properties. Work with the silicone resins had previously been discontinued because they formed a gel when milled with a large majority of frits believed suitable for use in this coating. This is not a problem when applying the frit and resin separately.

Several frit compositions were milled with water and sprayed on steel strips for firing in the gradient furnace. The following two compositions began to fuse between 900° and 950° F and formed a smooth continuous coating to 1500° F.

Composition No. 1	Composition No. 2
80 parts Frit No. 231	60 parts Frit No. 231
20 parts Frit No. 8101	20 parts Frit No. 8101
10 parts -325 mesh Al_2O_3	20 parts Frit No. 3E46R
50 parts water	50 parts water

All other compositions burned out before reaching 1500° F or did not fuse until 1100° F. Strips were coated with the above two compositions, dried, coated with Dow Corning 840 resin and cured. Upon firing in the gradient furnace for 10 minutes, the surface from 900° F to 1500° F had a rough blistered appearance. The strips were then placed in a furnace at 900° F and the temperature increased up to 1100° F and held for one hour. The coating fused down and the blistered area tended to smooth out.

3. Inorganic Sealers for Anodized Aluminum Wire

Available published data indicate that an insulation system consisting of aluminum oxide and amorphous silica should not be as dependent on temperature as other systems. Table VI gives some of the electrical properties of silica and alumina. Table VII gives some properties of lightly anodized 12.6-mil wire.

The amorphous silica should be deposited in the pores of the aluminum oxide coating in a thin layer so that the system is sealed against moisture, but the colloidal silica should not be deposited so heavily as to clog the pores of the system, thus causing it to lose flexibility.

Attempts were made to deposit colloidal silica in the pores of the aluminum oxide coatings by electrophoresis. Deposition was attempted from an aqueous dispersion of colloidal silica; however, gassing at the electrodes kept the particles from being deposited in the pores. Deposition of colloidal silica from an organic medium gave much better results. The procedure used for the deposition of the colloidal silica from the organic medium is as follows. The anodized wire to be coated was immersed in the solution as the anode with an aluminum wire of the

same size serving as the cathode. A d-c voltage was applied and the negatively charged silica particles migrated to the anode. As the concentration of the silica built up on the wire, the silica gelled. After the wires were removed from the solution, they were heated to 1000° F and held at that temperature for one hour to make them nonhygroscopic. Electrical properties of the wires were then measured.

TABLE VI

ELECTRICAL PROPERTIES OF ALUMINUM OXIDE AND AMORPHOUS SILICA

Composition	Temperature (° C)	Dielectric Constant (Frequency 10^{10})	Loss Factor (Frequency 10^{10})	Volume Resistivity (Ohm-Cm)
Al_2O_3	14	---	---	1×10^{16}
	25	8.8	---	---
	100	---	---	---
	250	---	---	---
	300	8.9	---	3×10^{13}
	350	---	---	---
	500	9.1	---	---
	800	---	---	3.5×10^{8}
	1100	---	---	1×10^{6}
SiO_2	25	3.78	0.0007	1×10^{15}
	100	---	---	---
	250	---	---	1×10^{12}
	300	3.78	0.0003	---
	350	---	---	1×10^{10}
	500	3.78	0.0003	---
	600	---	---	7×10^{6}
	1300	---	---	4×10^{5}

TABLE VII

TEST DATA FOR LIGHTLY ANODIZED 12.6-MIL PERMALUSTER WIRE[†]

Temperatures (° C)	Insulation Resistance (Ohms)	Dielectric Breakdown (Volts)
200	4.6×10^{9}	241
350	4.0×10^{8}	221
600	7.0×10^{7}	237

[†]General Electric Test Data on Permaluster Wire, by Henry Walker, presented in the paper, "High Temperature Aluminum Oxide Insulation for Electrical Wire and Strips," at the Electro Chemical Society Meeting in New York, April 28, 1958.

4. Wire Coatings for One Time Use Only

In missiles and rockets there may be a limited need for an electrical insulating coatings that would be expended after being used once. Since the missile or rocket would be used only once, the electrical wiring would have to survive only one temperature rise.

Work with a "one time at temperature coating" has produced very good results thus far. Anodized aluminum wires were coated with silicone resin and cured at 400° F. After curing, the wires were fired by raising the temperature in 100° F increments each hour. A series of wires were removed after each 100° F increment. Wires were fired and checked for electrical properties at 100° increments from 400° to 900° F. Flexibility of all wires was very good. The fired wires could be bent around a mandrel 26 times the diameter of the wire before any cracks were visible under a 10-power microscope and could be bent around a mandrel 16 times the diameter of the wire before electrical breakdown in a sodium chloride solution. See description of these tests under Section C, Parts 2 and 3.

C. Electrical and Physical Measurements

1. Dielectric Constant and Dissipation Factor

Samples of anodized aluminum wires were coated with Frit Composition Y listed in Table III with the exception that allyl glycidyl ether was substituted for the acetone. These samples were cured and shipped to the University of Illinois for electrical measurements. The results of this testing appear in Table VIII. Since these wires were prepared as individual samples, the thickness of the frit-resin coating varied considerably from sample to sample, making accurate checking of the dielectric constant difficult. (K is directly proportional to thickness.) See Table IX. The K value was therefore reported by the University of Illinois as a maximum and minimum value. At 400 cycles, all of the coatings had dissipation factors too high to permit balancing of the bridge; therefore, these measurements were made at 100 kilocycles only. The wide range of dissipation factor values would seem to indicate pinhole type defects rather than variation in the composition of the coating.

Additional samples of the coating of the type tested by the University of Illinois were prepared and the electrical properties determined in our laboratory. In order to have a simple facility for screening wire specimens for electrical properties of insulating coatings prior to shipping wires to the University of Illinois, a sample holder was constructed (see Figure 11). This sample holder is plugged into a "Q" meter; the parameters Q and C are measured and from these data the desired parameters are calculated by the following formula:

$$K = \frac{4.45 \times C \times t}{a} \qquad D = \frac{100 \times C_1 (Q_1 - Q_2)}{(C_1 - C_2)(Q_1)(Q_2)}$$

where K = dielectric constant
C = capacitance in μμfarads
t = thickness in inches
a = area square inches
D = dissipation factor per cent.

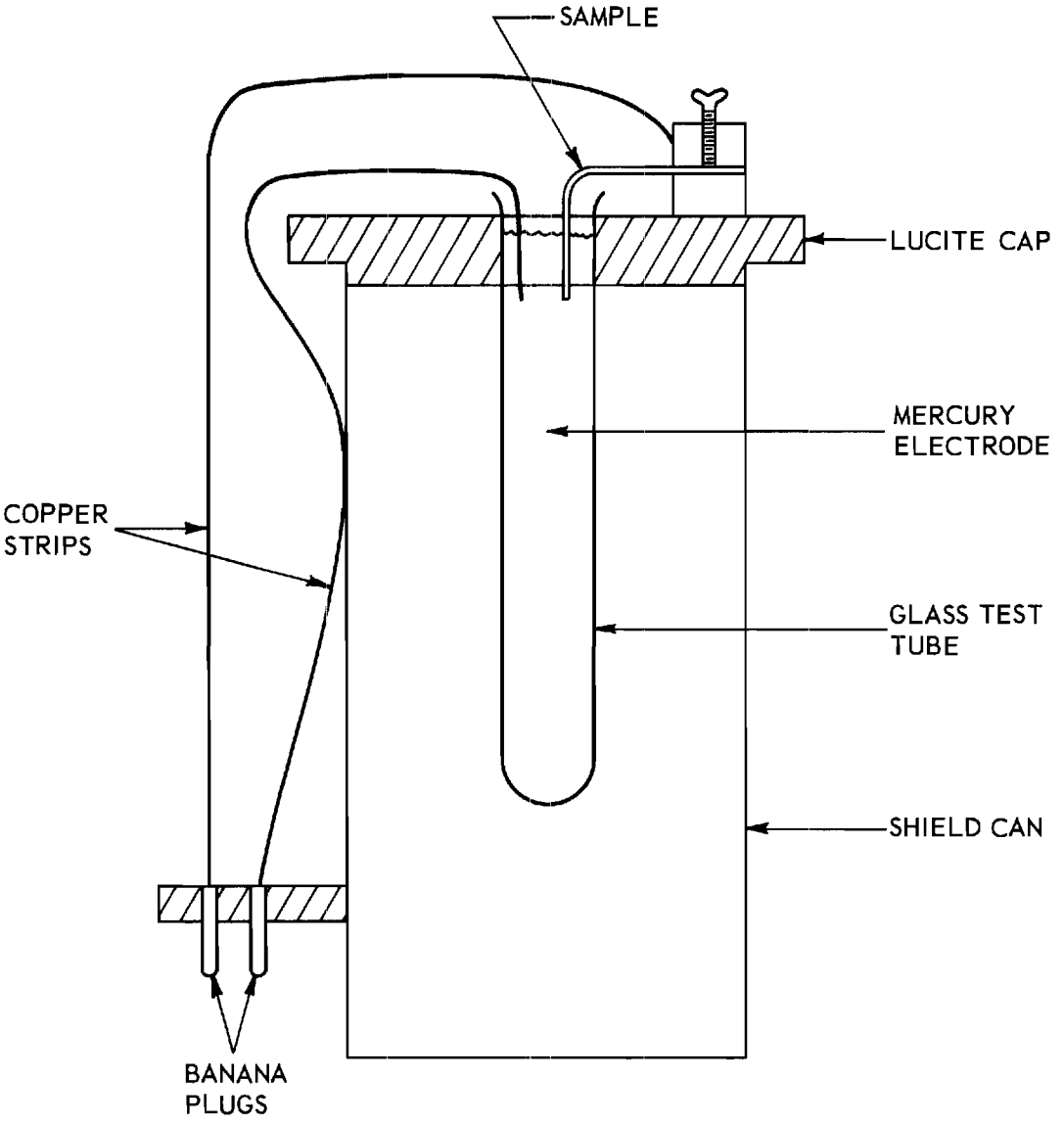

Figure 11. Sample Holder for Making Dielectric Measurements.

The procedure followed has been to set a predetermined frequency on the Q meter. Then by adjusting the capacitance, the resonant point is found. This gives a value for Q_1 and C_1. The sample holder is then placed in position on the Q meter and a sample is placed in it, at a proper depth in the mercury. The resonant point is again located by varying the capacitance and values for Q_2 and C_2 are obtained.

TABLE VIII

ELECTRICAL PROPERTIES OF ANODIZED ALUMINUM WIRE SEALED WITH FRIT-RESIN COATING Y (DETERMINED BY UNIVERSITY OF ILLINOIS)

Sample No.	Length of Sample (Inches)	Thickness of Coating Max. (Mils)	Thickness of Coating Min. (Mils)	F (Kc)	K Max.	K Min.	D (%)
1a	1.4	1.55	1.15	100	24.0	18.0	3.3
2a	2.2	2.60	1.95	100	12.2	9.3	5.1
3	3.4	3.65	2.85	100	21.0	16.8	34.1
3a	3.1	4.20	3.80	100	10.9	10.0	16.9
4	3.1	3.00	2.15	100	16.5	12.1	7.2
4a	3.4	2.50	1.85	100	14.0	10.5	6.3
5	3.5	2.50	2.05	100	12.8	10.6	13.2
5a	3.2	2.35	1.80	100	13.4	10.4	14.4
6	3.7	3.50	2.80	100	10.9	8.9	15.84
6a	3.4	3.30	2.75	100	13.2	11.2	18.1
7	3.6	3.30	2.30	100	11.8	8.4	15.45
7a	3.2	3.25	2.50	100	13.3	10.4	16.3
8	3.2	3.05	2.30	100	13.8	10.6	15.2
8a	3.3	3.60	2.50	100	10.0	7.6	8.2
10	3.1	3.15	2.35	100	11.6	8.9	12.05
10a	3.5	3.00	2.25	100	11.4	8.7	6.9
11	3.1	2.60	2.15	100	11.6	9.7	10.64
11a	3.2	3.05	2.55	100	9.9	8.4	7.3
12	2.8	2.65	2.15	100	12.0	9.9	15.8
12a	3.4	3.00	2.65	100	10.6	9.4	13.0

TABLE IX

ELECTRICAL PROPERTIES OF ANODIZED ALUMINUM WIRE SEALED WITH FRIT-RESIN COATING Y (DETERMINED BY GEORGIA TECH)

Sample No.	Frequency (Kc)	Thickness of Coating (Mils)	D (%)	K
1	152	2.35	8.14	10.1
1a	152	3.25	10.7	11.35
1a	158	3.25	11.2	10.5
2	159	1.65	6.74	9.9
2	152	1.65	---	---
3	152	1.75	---	10.5
3	159	1.75	12.9	10.0
3a	158	2.55	10.9	12.9
3a	152	2.55	15.3	13.5

Note: All samples were 0.75 inches in length.

In preparing samples, wires were measured with a micrometer in order to determine the thickness of coating. The cut ends of the wires were sealed with wax. All measurements were made at room temperature. Table IX lists the results of this test. These samples were similar to the samples sent to the University of Illinois.

Table X lists the results obtained from tests on anodized aluminum wire impregnated with colloidal silica. The values obtained for dielectric constant and dissipation factor were much lower than those obtained with the frit-resin coatings.

Table XI lists the electrical properties of Composition 1-1001.

Composition 1-1001

100 parts 3419 frit
50 parts Dow Corning Resin 806A
10 parts allyl glycidyl ether

The dielectric constants here are somewhat lower than those exhibited by Composition Y although the flexibility of this coating was not as good as that of Composition Y.

TABLE X

ELECTRICAL PROPERTIES OF ANODIZED ALUMINUM WIRE
SEALED WITH COLLOIDAL SILICA

Sample No.	Voltage	Time (Sec)	Thickness of Coating (Mils)	Length of Sample	f (Kc)	K	D (%)
1	30	15	3.2	0.75	220	5.60	1.52
1a	30	15	2.7	0.75	220	6.41	1.34
2	30	15	2.7	0.75	220	5.65	1.09
2a	30	15	2.5	0.75	220	5.45	1.18
3	30	15	2.7	0.75	220	4.10	0.837
4	100	10	3.5	0.75	220	4.95	0.569
4a	100	10	2.7	0.75	220	4.64	0.858
5	100	10	3.1	0.75	220	5.44	1.32
5a	100	10	3.2	0.75	220	5.90	0.67
6	100	10	3.5	0.75	220	7.93	0.77
6a	100	10	3.2	0.75	220	8.06	0.58
7	0	10	0.85	0.25	150	0.75	3.04
8	10	10	0.55	0.125	150	1.14	4.55
9	20	10	0.50	0.125	150	.61	6.57
10	30	10	0.65	0.125	150	.73	7.77
11	40	10	0.75	0.125	150	.56	16.70
12	50	10	0.75	0.125	150	.74	19.00
13	60	10	0.45	0.125	150	----	----
14	70	10	0.55	0.125	150	.70	6.76
15	80	10	0.40	0.125	150	.71	10.2
16	100	10	0.45	0.125	150	----	----
17	110	10	0.20	0.125	150	.46	8.47
18	120	10	0.70	0.125	150	2.66	12.20
19	130	10	0.35	0.125	150	.57	15.40
20	120	60	0.40	0.50	150	.34	2.50

TABLE XI

ELECTRICAL PROPERTIES OF ANODIZED ALUMINUM WIRE
SEALED WITH FRIT-RESIN COMPOSITION 1-1001

Sample No.	Frequency (Kc)	Thickness of Coating (Mils)	D (%)	K
1	220	2.35	1.66	8.3
1a	220	2.2	0.72	7.01
1b	220	1.55	----	----
1c	220	2.15	0.787	6.93
2	220	1.9	----	----
2a	220	2.2	0.850	7.96
2b	220	1.75	----	----
2c	220	2.05	1.095	7.04

Notes: 1. All measurements were made with Heath Kit "Q" meter.
2. All samples were 0.75 inches in length.

TABLE XII

ELECTRICAL PROPERTIES OF ANODIZED ALUMINUM WIRE
SEALED WITH SILICONE RESINS

Coating	Thickness of Coating (Mils)	Temperature to Which Subjected (° F)	Time (Hr)	Frequency (Kc)	Length (Inches)	K	D (%)
806 A	1.95	400	1	150	0.75	0.80	1.40
806 A	2.45	500	1	150	0.75	1.05	1.14
806 A	1.55	600	1	150	0.75	0.71	1.19
840	0.80	400	1	150	0.75	0.46	1.29
840	1.65	500	1	150	0.75	0.82	0.46
840	1.80	600	1	150	0.75	0.39	0.52
806 A	3.60	400	24	150	0.75	0.46	3.05

TABLE XIII

FLEXIBILITY OF ANODIZED ALUMINUM WIRE SEALED WITH SILICONE RESINS

Coating	Thickness of Coating (Mils)	Temperature to Which Subjected (° F)	Time (Hr)	Mandrel-to-Wire Ratio at Which Coating Cracks	Mandrel-to-Wire Ratio at Which Coating Flakes Off Wire
806 A	1.95	400	1	30	22
806 A	2.45	500	1	30	12
806 A	1.55	600	1	26	< 8
840	0.80	400	1	30	< 8
840	1.65	500	1	30	8
840	1.80	600	1	26	< 8

In work with a coating to be used one time only, electrical measurements were made on silicone-resin-coated wires fired to various temperatures. The results here show that with only a minor development effort a coating for one time use could be easily achieved. (See Table XII).

2. Continuity of Coatings

A continuity test similar to that used by the University of Illinois has been used to check continuity of coatings. A polyethylene trough is filled with a sodium chloride solution. A tungsten wire in the sodium chloride solution serves as the positive electrode and the insulated wire to be tested for continuity is inserted as the negative electrode. A d-c potential is applied to the system and the insulated wire observed under a low power microscope for gas bubbles.

3. Flexibility Measurements

Flexibility of coated wires has been measured by use of a stepwise mandrel. The wire to be tested for flexibility is wrapped around the largest diameter of the mandrel and observed under a microscope for cracking. If no cracking is observed the wire is wrapped around succeedingly smaller diameters until cracking of the coating is observed.

The bent wire is also subjected to the continuity test described previously after bending around each step of the mandrel. Tests conducted thus far have shown that the anodized aluminum wires sealed with colloidal silica and the anodized wires coated with silicone resins have the best flexibility characteristics. Table XIII above shows the results of flexibility tests on anodized aluminum wires sealed with silicone resins and Table XIV shows the results of tests on anodized aluminum wires sealed with colloidal silica.

TABLE XIV

FLEXIBILITY OF ANODIZED ALUMINUM WIRE SEALED WITH COLLOIDAL SILICA

Sample No.	Thickness of Coating (Mils)	Voltage	Time (Sec)	Mandrel-to-Wire Ratio at Which Coating Cracks	Mandrel-to-Wire Ratio at Which Coating Flakes Off Wire
7	0.85	0	10	22	8
8	0.55	10	10	26	8
9	0.50	20	10	22	8
10	0.65	20	10	17	8
11	0.75	40	10	30	12
12	0.75	50	10	26	12
13	0.45	60	10	22	8
14	0.55	70	10	12	8
15	0.40	80	10	26	12
16	0.45	90	10	26	12
17	0.20	100	10	26	<8
18	0.70	110	10	17	8
19	0.35	120	10	26	8

FUTURE WORK

Work thus far indicates definite possibilities for frit - silicone resin sealing compositions and for the use of colloidal silica impregnation as a sealing medium for aluminum oxide coatings. Aluminum-clad copper wire with a barrier layer of silver had been received in continuous lengths in sufficient quantities to allow long lengths of wire to be coated continuously. By continuously coating wires, the thickness of insulation applied to wire can be controlled much more closely.

Wire sizes received are 0.045 inch, 0.0201 inch and 0.010 inch in diameter. These wires will be anodized and sealed by the use of frit - silicone resin coatings and by the use of colloidal silica impregnation. Wire coatings will be tested for flexibility and given the electrical screening tests described in this report. Insulated wires showing the most promise will be shipped to the University of Illinois for complete electrical testing.

AD Georgia Institute of Technology, Engineering Experiment Station, Atlanta, Ga., HIGH-TEMPERATURE INSULATION FOR WIRE, by J. N. Harris and J. D. Walton. February 1959. 34p. incl. illus. (Proj. 7350; Task 73500) (WADC-TR-58-13) (Contract AF 33(616)-3944) Unclassified report Aluminum was plated and subsequently anodized on substrates of copper, chrome, iron and Inconel. Efforts to anodize aluminum plated over various (over)	UNCLASSIFIED UNCLASSIFIED
AD layer metals on copper were unsuccessful. Frit-silicone resin compositions were applied to anodized wire in separate steps, and electrical properties of frit-resin coatings applied to anodized wire were determined. Colloidal silica was deposited electrophoretically on anodized aluminum as a possible substitute for frit-resin coatings. Work on a "one time at temperature coating" showed possibilities of continuous operation to 900° F.	UNCLASSIFIED UNCLASSIFIED

CATALOG CARDS

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WADC TECHNICAL REPORT 58-13
PART III
ASTIA DOCUMENT NO.

HIGH-TEMPERATURE INSULATION FOR WIRE

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ATLANTA, GEORGIA

MARCH 1960

Materials Laboratory
Contract No. AF 33(616)-3944
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WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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MARCH 1960

WRIGHT AIR DEVELOPMENT DIVISION

FOREWORD

This report was prepared by the Engineering Experiment Station of the Georgia Institute of Technology under USAF Contract No. AF 33(616)-3944, Supplemental Agreement No. 4(59-833). This contract was continued under Project No. 7371, "Electrical and Electronic Materials," Task No. 73710, "Electrical and Electronic Inorganic Materials." The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Lt. J. M. Kacicz, Jr. acting as project engineer.

This report covers work conducted from March 1959 to March 1960. Included is a brief summary of the first two years of effort.

ABSTRACT

Normal anodizing of commercial aluminum-clad copper wire did not result in complete anodization of the aluminum due to its thickness. Advantage was taken of the solvent action of sulfuric acid to remove a portion of the excess aluminum, however, complete anodization was not possible due to uneven removal of the aluminum causing exposure of the copper. Best results obtained were an anodized coating thickness of 0.8 to 1.0 mils and an unanodized aluminum layer 0.3 mil in thickness.

The use of electrophoretic deposition of colloidal silica for sealing the pores of anodized coatings was not successful. Better results were obtained by providing colloidal silica sealing by gelling hydrolyzed ethyl silicate solutions on phosphoric acid anodized wire. This resulted in a wire insulation with an average dielectric constant of 2.89 and a dissipation factor of 1.87 per cent.

The best insulation system was provided by sealing sulfuric acid-magnesium chloride anodized wire with a frit-resin coating. This wire was capable of operating at 800°F.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

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INTRODUCTION

The ever increasing speeds developed and anticipated by air and space vehicles are creating higher and higher ambient temperatures. Electrical components operating under these higher temperature conditions are seriously handicapped by the lack of suitable insulating materials.

The development of an electrical wire insulation for service use between -85° and 1500°F has been the objective of this contract. This report covers the third year's work on the project initiated on February 1, 1957.

The objectives of this program for the development of high temperature wire insulation have been as follows:

1. High dielectric strength
2. Low loss tangent
3. Low dielectric constant
4. Sufficient flexibility at room temperature to allow the coated wire to be wrapped around a mandrel ten times the diameter of the wire
5. High impact strength
6. High abrasion resistance
7. Pressure change resistant
8. Thermal shock resistant
9. Corrosion resistant to oils and salty atmosphere
10. Low strategic material content
11. Minimum weight
12. Maximum imperviousness to moisture
13. Maximum reflectivity
14. Concentricity of coating
15. Life expectancy of at least 10,000 hours

A. Background

The greatest need for flexibility of a wire insulation would be during installation at room temperature. The approach taken by Georgia Tech was to combine an organic and an inorganic coating in the form of a resin containing a powdered glass filler, the resin providing the necessary initial flexibility. Once this insulation system is heated up, the resin should burn out and the powdered glass filler should fuse forming a continuous coating to 1500°F. At 1500°F, however, a vitreous enamel coating would have poor electrical properties unless a stand-off insulator were provided to keep the viscous molten coating from contact with the bare wire. A refractory base coating would provide this stand-off insulator. Aluminum oxide in the form of an anodized coating was selected as the most promising stand-off insulator because of its dielectric properties and its ability to flex upon bending.

B. Results of Previous Work

The first two years work on this contract was described in detail in WADC Technical Report 58-13, Parts I and II. The significant results of this work are as follows.

Equipment was developed for plating of aluminum on copper substrates from

an ethereal solution of lithium aluminum hydride. Coatings of aluminum suitable for anodizing were obtained directly on copper wire but efforts to plate aluminum over barrier layer metals applied to copper such as chrome and iron were unsuccessful.

Since the problem of producing continuous lengths of suitable aluminum-coated wire was so great and since two commercial manufacturers were producing aluminum-clad wire with barrier layer metals between the copper and the aluminum, this phase of the study was discontinued. This allowed a greater amount of time to be placed on anodizing of coatings.

Anodized coatings obtained by the use of phosphoric-acid-electrolyte proved superior to all other coating techniques investigated. These coatings proved to be very flexible and had good electrical properties. The coatings obtained could be bent around a mandrel less than ten times the diameter of the wire as required by the contract.

Early work with ceramic organic coatings as sealers for refractory base coatings indicated greater flexibility for epoxy resin coatings in combination with porcelain enamel frits than for silicone resin - porcelain enamel frit combinations. Epoxy resins were found to be more compatible with a greater number of porcelain enamel frits than the silicone resins. However, because of the higher burn out temperature and better dielectric properties of the silicone resins they were selected for further work.

The best results obtained in sealing anodized coatings was by the use of colloidal silica. Much lower dielectric constants were obtained with this type of system but the wide range in dissipation factor indicated pinhole type defects. Flexibility of the colloidal silica-impregnated wires was good although cracking of the coatings was observed when they were bent around a mandrel 20 times the diameter of the wire; in most cases electrical breakdown did not occur with the first cracking.

A wire coating for one time use (in a missile or rocket) could possibly be achieved by coating an anodized wire with a silicone resin. The resin would provide low temperature protection from moisture. At higher temperatures the resin would burn out but at these temperatures the moisture problem would be non-existent.

SUMMARY

A. Base Coatings

The inability to obtain thin, uniformly coated aluminum-clad wire for anodizing has been the major difficulty throughout this contract. The coatings obtained with both phosphoric acid and sulfuric acid--magnesium chloride electrolytes have been satisfactory except for the inability to completely convert all of the aluminum on the wire to alumina. The phosphoric anodized wires have been found most desirable due to their flexibility; however, the greater depth of anodizing due to the solvent action of sulfuric acid electrolyte caused it to be selected for the majority of the work during the past year. The lesser flexibility of the

sulfuric-acid-anodizing has not been a handicap since the flexibility of the alumina coating formed by this anodizing is better than the flexibility of the sealing coatings applied to it. Sulfuric-anodized coatings 0.8 to 1.0 mil in thickness have been obtained on 0.0201 inch diameter wire. The remaining unanodized aluminum on this wire is less than 0.3 mil in thickness yet diffusion of this aluminum into the copper at temperatures above 1000°F causes the wire to become very brittle. At least one commercial manufacturer of anodized aluminum-clad wire claims operations to 1900°F due to the barrier layers of nickel and silver between the aluminum and copper. All wire anodized by Georgia Tech has had barrier layers of nickel and silver; however, these have not prevented diffusion of unanodized aluminum into the copper at temperatures of 1000°F and higher.

B. Sealing Coatings

The use of colloidal silica as a sealer for anodized wire was not successful due to the extremely small pore size of anodized coatings and the difficulty of causing the particles of colloidal silica to enter these pores. Much greater success was obtained by allowing ethyl silicate, a true solution, to enter the pores of the coating. Then by gelling the ethyl silicate, particles of silica are formed which remain in the pores. Much better results were obtained with phosphoric-acid-anodized wire than with sulfuric acid--magnesium chloride anodized wire because of the inability to fill the smaller pores of the sulfuric acid anodized coating with silica particles.

The best insulation system was obtained by sealing sulfuric acid--magnesium chloride anodized wire with a frit-resin coating consisting of one part 3419 frit to 2 parts Dow Corning 806A Resin. This insulation system is capable of operating for many hours at 800°F.

EXPERIMENTAL WORK

A. Base Coatings

1. Anodizing Equipment

The experimental work during the past year was devoted to producing sealed wire systems in continuous lengths. A large portion of work was carried out in obtaining suitable anodized coatings on continuous lengths of anodized wire.

In order to carry out this work the 7- by 8- by 16-inch lead lined tank previously used for anodizing wire lengths up to 16 inches was modified to anodize wire continuously. This modification consisted of adding a lucite rack and pulleys to the tank in order to lead the wire continuously through the anodizing bath. The rack was designed so that 80 inches of wire were submerged in the electrolyte at one time. (See Figure 1). Two drive mechanisms were fabricated so that wire could be drawn through the electrolyte at rates of 1.63 and 4 inches per minute. The electrolyte was agitated by air stirrer motors. Anode contact is maintained through the metal feed spool and cathode contact is provided by the lead lining of the tank. A thermostatically controlled immersion heater provides

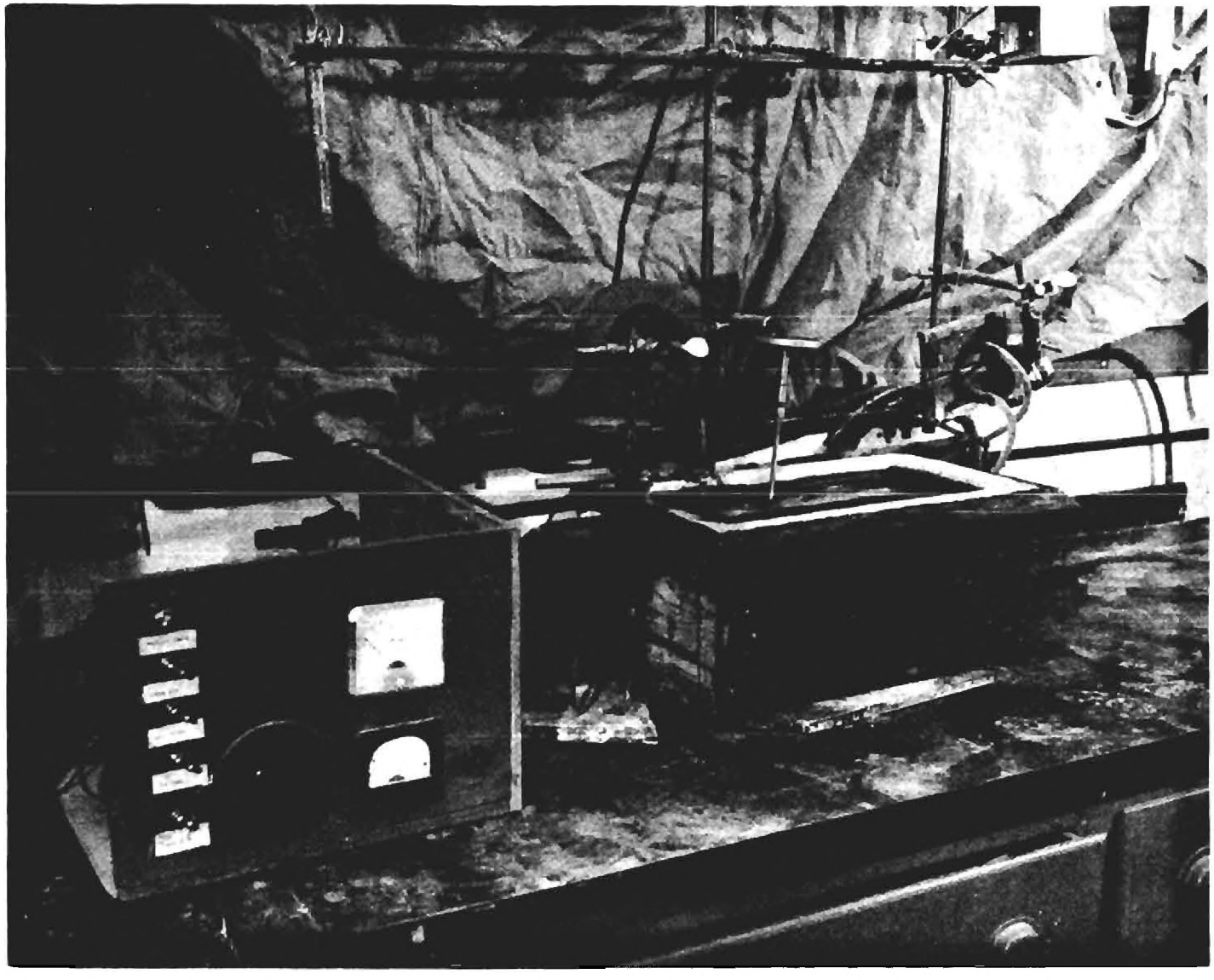

Figure 1. Modified Anodizing Equipment.

a constant temperature for the electrolyte. After leaving the bath the anodized wire is cleaned by a spray of water and dried by a stream of air. The first wire anodized with this continuous system was 0.0201 inch aluminum-clad wire obtained from the Westinghouse Electric Corporation. The wire was pulled through the electrolyte at a rate of 1.63 inches per minute and had a total time in the electrolyte of 50 minutes. The wire was anodized in a 4 per cent (by weight) phosphoric-acid-electrolyte maintained at a temperature of 45°C. A potential of 100 volts d-c was maintained on the wire. The final diameter of this wire was 0.0206 inch. The depth of anodizing was 0.00028 inch and the thickness of the aluminum coating was 0.00207 inch. Dielectric measurements on this wire were made and the dielectric constant and dissipation factor determined. Values obtained were: dielectric constant 0.787 and dissipation factor 5.02 per cent. Cracking of this coating was observed at a mandrel-to-wire ratio of 30 to 1. Flaking of the coating was observed at a ratio of 10 to 1.

Wire of 0.010 inch diameter with an aluminum coating of 0.0009 inch was anodized to a depth of 0.00024 inch. Some difficulty was encountered in andoizing this wire due to pin holes in the aluminum coating causing localized heating which resulted in the wire breaking. Mechanical breakage also occurred due to tension in the feed system being too great. Due to these difficulties and the fact that the contract called for work with larger wire sizes no further work was carried out with 0.010 inch diameter wire.

2. Aluminum-Clad Wire

The major problem faced throughout this contract has been the acquisition of suitable aluminum-clad copper wire. Experience has shown that alumina coatings 0.0003 to 0.0005 inch in thickness are desired. Thicker coatings of alumina do not have the desired flexibility. The thickness of the aluminum-cladding on the 0.0201 inch diameter wire obtained from Westinghouse has been approximately 0.0028 inch in thickness. If all of this aluminum was converted to alumina by anodizing, it would take extremely high current densities and long anodizing times and would produce a coating with little or no flexibility. Since at this time no other wire was known to be available, efforts were made to remove a portion of aluminum from this wire.

a. Stripping of Aluminum-Clad Wire. Several possible stripping solutions were investigated to determine if a part of the aluminum could be removed and the remaining aluminum on the copper wire still remain concentric and free from pits so that it was suitable for anodizing. Table I shows the stripping solutions investigated and the results obtained.

The best results were obtained with the use of the phosphoric-acid-stripping solution in that the aluminum was removed smoothly from the wire with very little pitting, thus a study was initiated to investigate the use of phosphoric acid as a stripping medium. The results of this work appear in Table II. Increasing current densities above 464 amps/ft^2 caused greater pitting of the aluminum and embrittlement of the wire as a result of the heat generated and the accompanying diffusion of aluminum into the copper. It was found that more even coatings with less pitting could be obtained with phosphoric-acid-stripping solutions if little or no current was used and that the rate of stripping of aluminum from the wire could be increased by heating the solution. The results of this study

TABLE I

SURVEY OF STRIPPING SOLUTIONS
FOR REMOVAL OF ALUMINUM FROM ALUMINUM-CLAD WIRE

Stripping Solution	Method of Treatment	Time in Solution (Minutes)	Results
10% Na OH (wt)	No agitation	3	Surface of wire etched with some pitting but wire could still be anodized
10% Na OH (wt)	No agitation	5	Ditto
10% Na OH (wt)	No agitation	9	Ditto
10% Na OH (wt)	D-C wire anodic 365 amp/ft^2	5	Wire pitted with pin holes reaching to copper
10% Na OH (wt)	A-C wire 360 amp/ft^2	5	Aluminum and copper severely eroded
18% H_3PO_4	A-C wire 464 amp/ft^2	20	Aluminum removed evenly from wire with slight pitting
Perchloric acid (2 pts by weight) Acetic anhydride (7 pts by wt.)	D-C wire anodic 46.5 amp/ft^2 agitation of solution	15	Pits in the aluminum
Perchloric acid (2 pts by weight) Acetic anhydride (7 pts by wt.)	D-C wire cathodic 46.5 amp/ft^2 agitation of solution	15	Pits in the aluminum

are shown in Table III. Continuous anodizing of wires stripped in phosphoric acid was not practical since frequent breaking of the wire took place while anodizing. This was believed to be due to selective etching by the hot phosphoric acid.

b. Sulfuric Acid Anodizing. The best method found for removing the excess aluminum from the available aluminum clad copper wire was to take advantage of an anodizing technique which removes some of the aluminum in the process of converting aluminum to alumina. In this anodizing process the thickness of the oxide coating is limited by the concentration of the electrolyte and the

TABLE II

USE OF PHOSPHORIC ACID WITH AN ALTERNATING CURRENT
FOR STRIPPING OF ALUMINUM FROM ALUMINUM-CLAD WIRE

Stripping Solution	Current Density (Amp/Ft^2)	Time in Solution (Min.)	Results
13% H_3PO_4 (wt.)	464	20	Very little aluminum removed, no pitting
13% H_3PO_4 (wt.)	696	20	Pitting of the aluminum coating
13% H_3PO_4 (wt.)	928	20	Aluminum still continuous but wire quite brittle
29% H_3PO_4 (wt.)	464	20	No improvement over 13%

TABLE III

USE OF HOT PHOSPHORIC ACID SOLUTIONS
FOR STRIPPING ALUMINUM FROM ALUMINUM-CLAD WIRE

Stripping Solution	Temperature (°C)	Time (Min.)	Amount of Aluminum Removed (Mils)	Results
5% H_3PO_4 (wt.)	80	15	----	Wire was evenly etched and anodized well
5% H_3PO_4 (wt.)	80	20	0.89	Some pitting, wire broke after 15 min. anodizing
5% H_3PO_4 (wt.)	80	30	----	No pinholes visible but wire broke after 15 min. anodizing
2% H_3PO_4 (wt.)	90	15	0.81	Wire was slightly pitted but anodized well
2% H_3PO_4 (wt.)	90	20	0.93	Evenly etched anodized well and was flexible
2% H_3PO_4 (wt.)	90	30	1.34	Wire was evenly etched but broke after 30 min. anodizing

current applied to the system. Some electrolytes such as sulfuric acid have an appreciable solvent action on the outer surface of the oxide film and dissolve some oxide therefrom. Thus, while anodizing in sulfuric acid with a constant current density, a maximum thickness of alumina will be built up. The sulfuric-acid-electrolyte will dissolve away the cuter oxide and additional aluminum will be converted to alumina to maintain a constant thickness.

In order to obtain faster anodizing in sulfuric-acid-electrolyte magnesium chloride was added. The magnesium chloride allows higher currents with lower voltages than are obtainable with sulfuric acid alone. The higher currents enable the anodizing process to proceed at a faster rate. This faster anodizing process is explained in an article by E. Herrmann.[1] In this article an electrolyte consisting of 20 per cent sulfuric acid and 3 1/2 per cent magnesium chloride was described. Better results were obtained in our work using 20 per cent by weight sulfuric acid containing 0.08 per cent by weight magnesium chloride.

The anodized films obtained with the sulfuric acid--magnesium chloride electrolyte are smooth and adherent. These films are comparable in electrical properties to those obtained with phosphoric-acid-anodizing but have thicknesses up to one mil and are not as flexible. These coatings flake off the wire at a mandrel-to-wire diameter of 12 to 1. As stated earlier in this report an anodized film 0.5 mil in thickness would provide good flexibility and dielectric properties. The lessened flexibility of these thicker anodized coatings may not be a problem at this stage of the art since the flexibility of the sulfuric anodized wire is better than the flexibility of the frit resin coatings applied to it.

A study was conducted to determine the amount of aluminum that could be removed by anodizing. Aluminum-clad wire of 0.0201-inch diameter was anodized in an electrolyte consisting of 20 per cent by weight sulfuric acid and 0.08 per cent by weight magnesium chloride. The results of this study appear in Table IV. The time of anodizing shown in the table was the maximum time that the wire could be left in the electrolyte without frequent breaking. The best results were obtained when the electrolyte temperature was kept below 100°F and the current density below 200 amps/ft^2. Higher current densities caused embrittlement of the wires.

Figure 2 is a photomicrograph of specimen No. 2 in Table IV. It can be seen from this figure that the unanodized aluminum varies from 0.3 to 0.8 mil and that the thickness of the anodized coating varies from 0.8 to 1.0 mil.

Longer anodizing times were tried but no further aluminum could be removed without breaking the wire. This breakage can probably be attributed to the lack of uniformity of the remaining aluminum coating on the wire. The lack of uniformity means that the thinner portions of aluminum will be converted to alumina and dissolved away by the solvent action of the sulfuric acid. The

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[1] E. Herrmann, "Anodizing Aluminum Wire and Strip by a Continuous Process," Metal Finishing 55, 82-83 (Nov. 1957), Abstracted from Metall 8, No. 17/18, 667 (Sept. 1954).

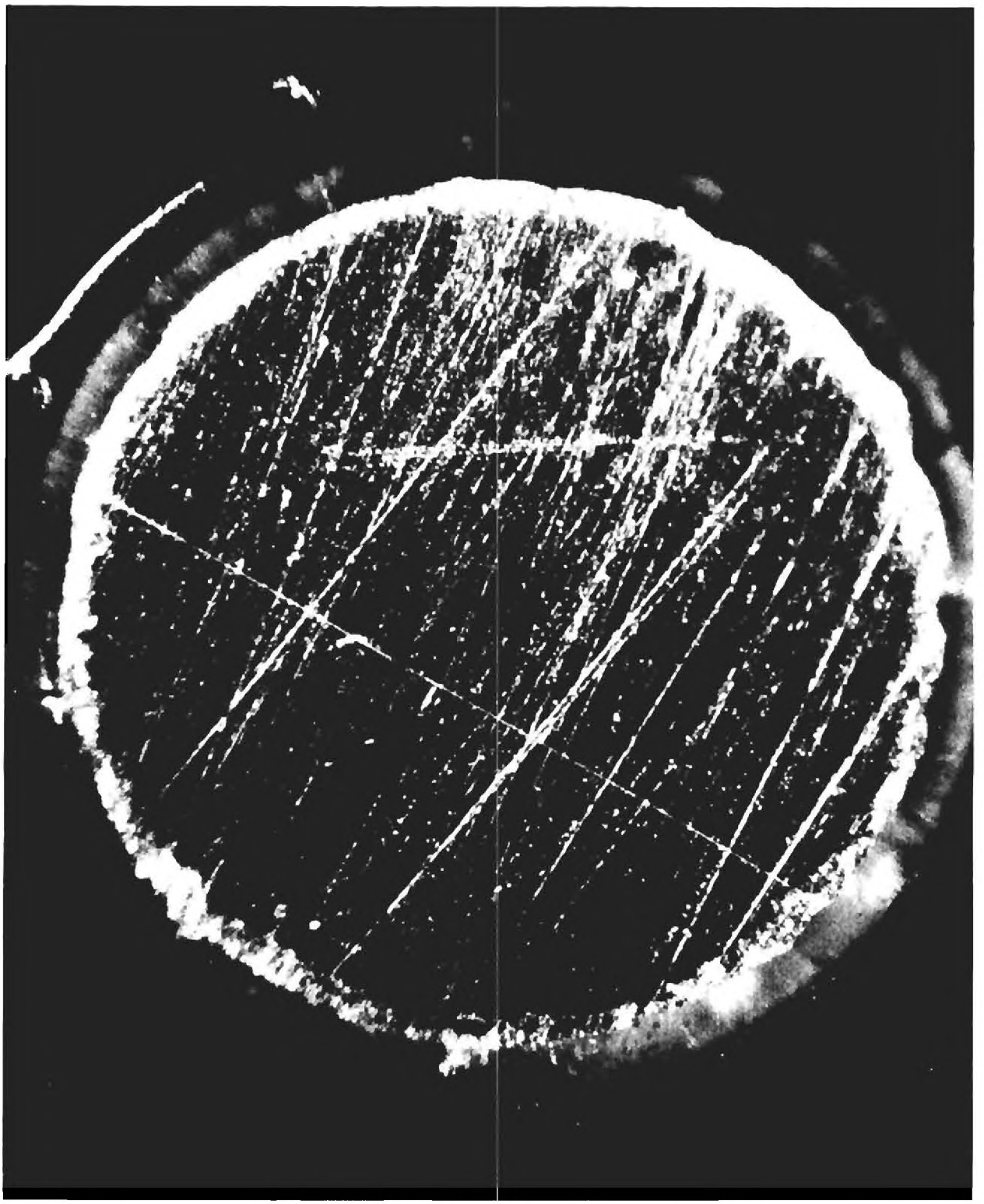

Figure 2. Photomicrograph of Aluminum-Clad Wire Anodized in Sulfuric Acid-Magnesium Chloride Electrolyte.

copper will therefore be exposed where the aluminum is thin. Since copper has a smaller coefficient of resistivity than aluminum, the greater current which is allowed to flow heats and breaks the wire where the copper is exposed.

TABLE IV

STRIPPING OF ALUMINUM
BY ANODIZING IN SULFURIC ACID ELECTROLYTE

Specimen Number	Temperature of Electrolyte (°F)	Current Density (Amp/Ft^2)	Wire Speed (In./Min)	Anodizing Time (Min.)	Average thickness of Remaining aluminum (Mils)
1	90	310	1.63	4.6	1.02
2	120	325	1.63	4.6	0.72
3	100	155	1.63	4.6	1.50
4	100	205	1.63	4.6	1.30
5	100	200	1.63	9.25	0.46

Note: In each case the average anodized coating thickness was 0.7 to 0.9 mil

Anodized coatings produced in phosphoric-acid-electrolyte build up more slowly than those produced by anodizing in sulfuric acid--magnesium chloride electrolyte, therefore, it was felt that the phosphoric-acid-anodizing process could be more closely controlled and further aluminum might be converted to alumina without breaking the wire. Aluminum-clad copper wire was anodized in sulfuric acid--magnesium chloride electrolyte until 0.7 mil or less of aluminum was left on the wire. Attempts were then made to strip the sulfuric-acid-anodized coating from the wire and to anodize the remaining aluminum in phosphoric-acid-electrolyte. This also met with little success due to continued breaking of the wire in the phosphoric-acid-electrolyte.

A new supply of 0.020 and 0.051 aluminum-clad copper wire was obtained from Sylvania Electric Products Incorporated to determine if this wire had a more uniform aluminum coating than the Westinghouse Wire. Preliminary anodizing studies on this wire indicated a more uniform aluminum coating in that less breaking of the wire was experienced due to eroding of the aluminum in one spot. Time or funds did not allow completion of this study.

B. Sealing Coatings

1. Colloidal Silica

Colloidal silica was applied by electrophoresis to phosphoric-acid-anodized wire of 0.0201 inch diameter by pulling the wire around a pulley submerged in DuPont Organosol colloidal silica then pulling the wire through a furnace at 1000° F. A 100-volt d-c potential was applied to the system with the wire as the anode and the colloidal silica container the cathode. The wire was coated with colloidal silica but every 4 to 5 inches the aluminum that was not anodized showed through the coating. It is believed that excess tension on the wire which resulted from the ratchet system caused the aluminum to pull apart in the hot zone of the furnace. Attempts were made to measure electrical properties of the coated wire in places where the coating did not appear to be broken, but the capacitance was too high, which would indicate that there were holes in the coating which could not be seen by the eye.

2. Ethyl Silicate

The pore openings in phosphoric anodized coatings are extremely small so that even with the use of colloidal silica deposition by electrophoresis difficulty may be encountered in forcing particles of silica into the pores. Ethyl silicate is a true solution and the surface tension is such that it readily wets anodized coatings and should penetrate into the pores of the coating. If solutions of ethyl silicate could be made to gel after wetting the coating, the silica would be left in the pores. Then by heating the wire to 1000° F the silica could be made non-hygroscopic.

A study of hydrolyzed solutions of ethyl silicate was initiated to determine at what pH gelling would take place and the effect of pH on gelling time. Tetraethyl orthosilicate and 2-per-cent-hydrochloric-acid were mixed by vigorous mechanical stirring until the mixture hydrolyzed. Ammonium citrate was then added to the hydrolyzed solution to act as a buffer and one-per-cent-ammonium-hydroxide added to adjust the pH. The solution was then diluted with five volumes of water.

Table V is a study of gelling time versus pH for hydrolyzed solutions of ethyl silicate diluted with water. Figure 3 shows the effect of pH on gelling time.

Anodized wire was passed through solution 5 of Table V until the solution gelled. Gelling time was 23 minutes; therefore, the first few inches of wire entered the furnace before the coating gelled. However, the solution on the greater part of the wire had gelled before entering the furnace. This method was not suited for continuous operation so it was felt that the solution could be caused to gel on the wire after the wire passed through the ethyl silicate solution. The electrical properties of the wire passed through solution 5 could not be checked with the Q meter because of high capacitance, indicating breaks or pin holes in the coating.

To allow a greater concentration of silica to be deposited on the anodized wire, concentrated solutions of tetraethyl orthosilicate were hydrolyzed and the

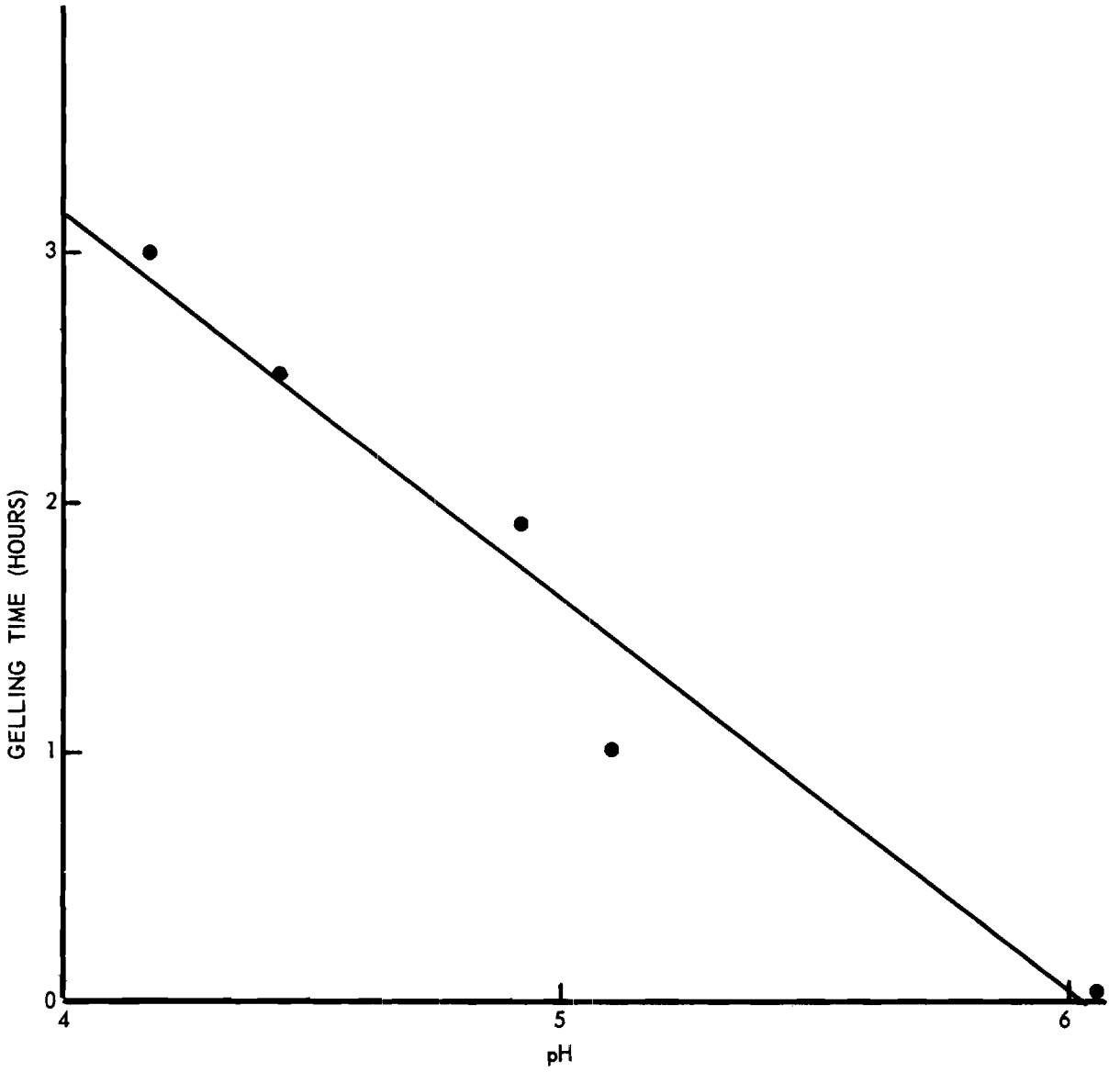

Figure 3. Gelling Time Versus pH for Diluted Hydrolyzed Tetraethyl Orthosilicate Solutions.

pH adjusted for proper gelling time. The following solution has a gelling time of greater than 10 hours which allows the coating operation to be carried out throughout the working day.

5 volumes tetraethyl orthosilicate
1 volume 2-per-cent-hydrochloric-acid
1.5 per cent (weight) ammonium citrate
4.5 per cent (weight) 1-per-cent-ammonium-hydroxide.

The pH of the above solution is 3.5. Since concentrated solutions are not as stable as diluted solutions, a lower pH is required to maintain a longer working time.

TABLE V

GELLING TIME VERSUS pH FOR DILUTE HYDROLYZED ETHYL SILICATE SOLUTIONS[+]

Composition	Ammonium Citrate Added (o/o)	One Per Cent Ammonium Hydroxide Added (o/o)	pH	Time to Gel (Hours)
1	0.28[++]	0.84[++]	4.2	3.0
2	0.47	0.84	4.4	2.5
3	0.47	2.0	4.9	1.9
4	0.47	3.0	5.1	1.0
5	0.47	7.0	-	0.38
6	0.47	14.0	6.1	0.05

[+]Solutions consisted of five volumes of tetraethyl orthosilicate, and one volume of 2 per cent hydrochloric acid. The hydrolyzed solution was then diluted with six volumes of water.

[++]Percentages in these columns based on weight of diluted hydrolyzed solution.

Anodized wire was coated by pulling it through the above solution and then through a one-per-cent-ammonium-hydroxide solution which gelled the coating almost immediately. Figure 4 is a diagram of the equipment used for applying the ethyl silicate coating. The wire was then passed through a gradient furnace which increased the temperature of the wire gradually from room temperature to 1000° F. The wire was pulled through the solution at a rate of 1.63 inches per minute. The distance between the last solution and the gradient furnace was

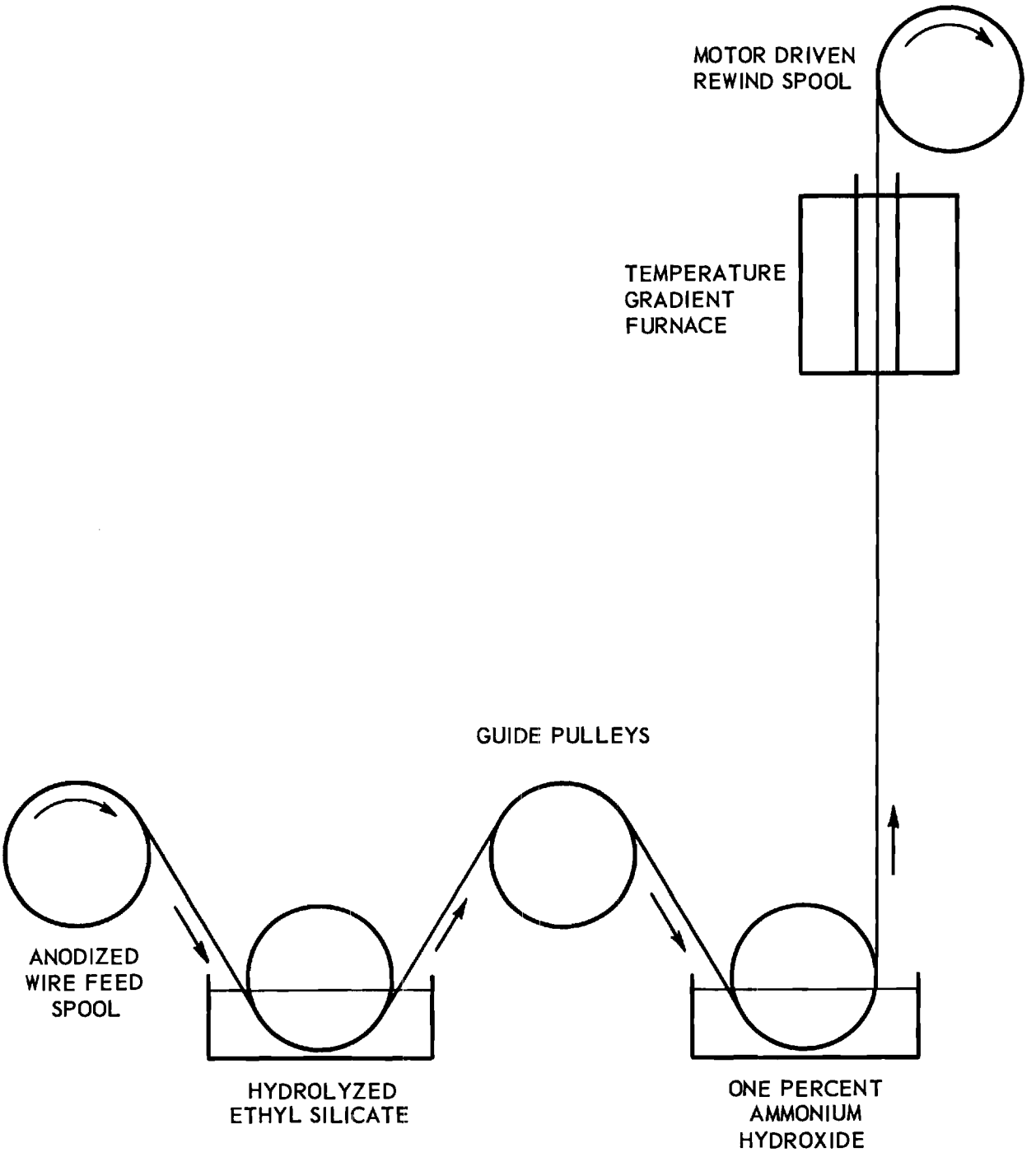

Figure 4. Schematic Sketch of Equipment for Continuously Sealing Wire with Hydrolyzed Ethyl Silicate.

sufficient to allow an air-drying time of 15 minutes before the wire entered the furnace.

In order to determine the weight of silica picked up in the pores of a phosphoric-acid-anodized wire the following work was carried out. A two foot length of 0.0201-inch diameter aluminum-clad wire anodized by the phosphoric-acid-process was carefully cleaned and weighed to the nearest 0.1 milligram. The wire was immersed in hydrolyzed ethyl silicate solution for one minute then dipped into a 2-per-cent-ammonium-hydroxide-solution for 15 seconds. The wire was air-dried for one hour, then dried at 60° C for an additional 15 minutes. After drying the wire was found to have picked up 0.0036 gram. The above procedure was repeated a second time and the wire was found to have picked up 0.0047 gram over the original weight.

To determine the weight of alumina on a 2-foot length of anodized wire, the wire was stripped to constant weight in the following boiling solution:

35 ml. of 85-per-cent-phosphoric-acid
20 gm. chromic acid
1000 ml. water

The average weight of alumina was found to be 0.0100 gram for the 2-foot length of wire. Thus the silica picked up in the pores of the anodized coating represents 32 per cent of the total weight of the insulation.

The above procedures were repeated with wires anodized in sulfuric acid--magnesium chloride electrolyte. A 2-foot length of 0.0201-inch diameter anodized wire was carefully cleaned and weighed to the nearest 0.1 milligram. The wire was immersed in a hydrolyzed ethyl silicate solution for one minute then dipped into a 2-per-cent-ammonium-hydroxide solution for 15 seconds. The wire was air-dried for one hour, then dried at 60° C for an additional 15 minutes. After drying the wire was found to have picked up 0.0015 gram. The above procedure was repeated a second time and the wire was found to have picked up a total of 0.0037 gram.

To determine the weight of alumina on a 2-foot length of 0.0201-inch diameter wire anodized in sulfuric acid--magnesium chloride electrolyte, the wire was stripped in the same solution used with phosphoric-acid-anodized wires. The average weight of alumina was found to be 0.0470 gram for the 2-foot length of wire. Thus the silica picked up in the pores of the anodized coating represents 7.8 per cent of the total weight of the insulation.

All wire coatings prepared were subjected to screening electrical measurements at Georgia Tech prior to sending promising specimens to the University of Illinois for more complete electrical testing. The measurements made at Georgia Tech were for room temperature dielectric constant and dissipation factor at 150 kilocycles and for continuity of the coating. Dielectric constant and dissipation factor were calculated from measurements of the parameters Q and C measured with a Q meter. These measurements were made using a fixture which allows the coated wire to be immersed in mercury thus assuring intimate contact with the insulation. (See Figure 5.) The wire serves as one electrode and the mercury as

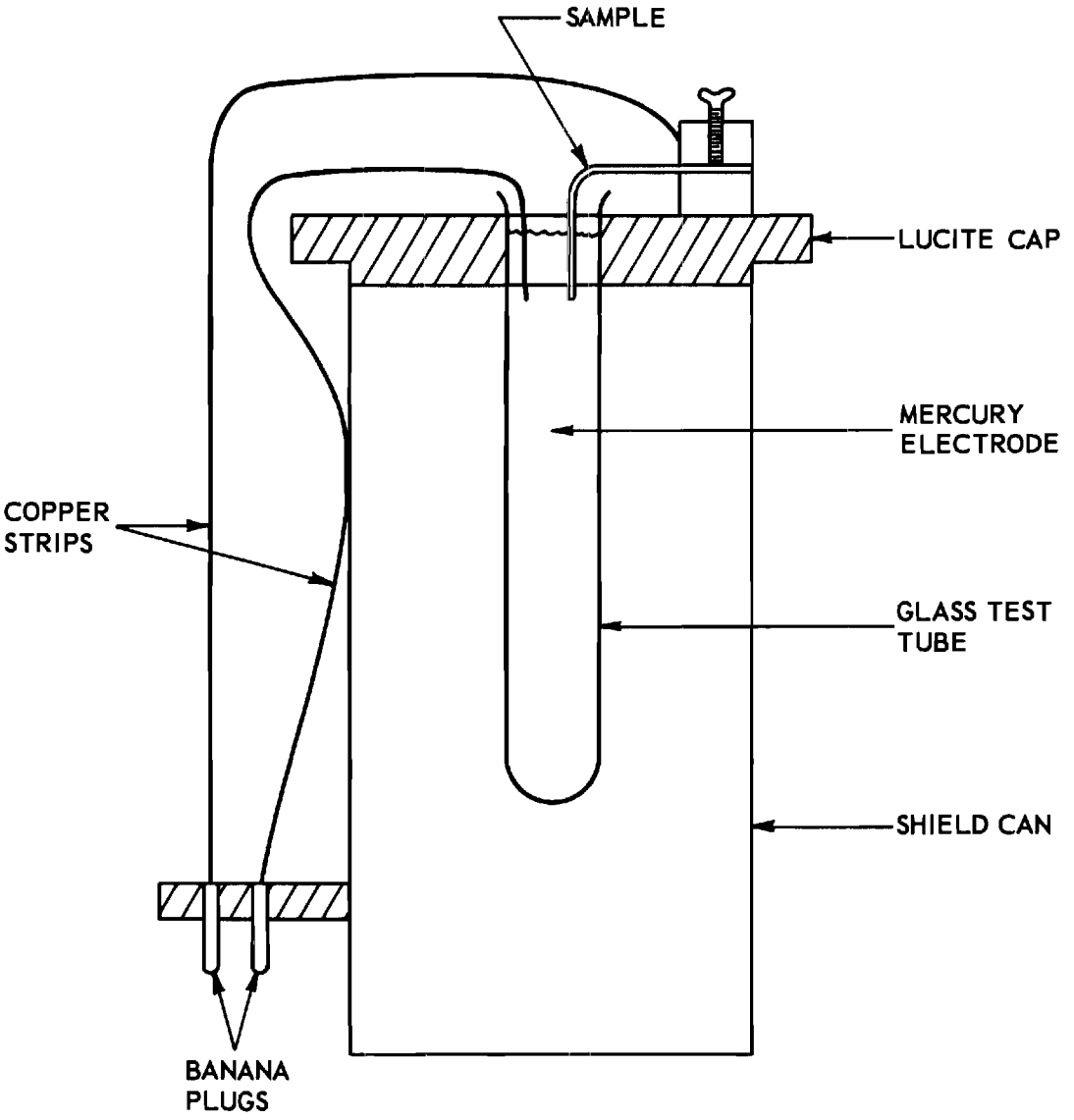

Figure 5. Sample Holder for Making Dielectric Measurements.

the other. The procedure followed is to set a predetermined frequency on the Q meter. Then by adjusting the capacitance, the resonant point is found. This gives a value for Q_1 and C_1. The sample holder is then placed in position on the Q meter and a sample is placed in it at a proper depth in the mercury. The resonant point is again located by varying the capacitance and values for Q_2 and C_2 are obtained. From these values dielectric constant and dissipation factor may be calculated using the following formulas:

$$K = \frac{4.45 \times C \times t}{a} \qquad D = \frac{100 \times C_1 (Q_1 - Q_2)}{(C_1 - C_2)(Q_1)(Q_2)}$$

where K = dielectric constant
C = capacitance in $\mu\mu$ farads
t = thickness in inches
a = area in square inches
D = dissipation factor per cent

To determine continuity the insulated wire to be tested is immersed as the negative electrode in a 10 per cent by weight sodium chloride solution. A platinum wire serves as the positive electrode. A d-c potential is applied to the system and the insulated wire observed under a 10 power microscope for gas bubbles.

In order to determine electrical properties of sealed phosphoric-acid and sulfuric acid--magnesium chloride anodized wires the following work was carried out. Continuous lengths of 0.0201-inch anodized-aluminum-clad wires were sealed by passing them through a solution of hydrolyzed ethyl silicate and then through a solution of one-per-cent-ammonium-hydroxide to gel the ethyl silicate on the wire. The dielectric properties of both types of sealed anodized wires are listed in Table VI.

The phosphoric-acid-anodized-ethyl silicate sealed wires were sent to the University of Illinois for determination of their electrical properties. These results appear in Tables VII and VIII. The dielectric strength measurements in Table VIII were obtained using a 2.24 inch mandrel over which the wire was draped during the test, thus subjecting the wire to approximately a 100:1 ratio of mandrel diameter to wire diameter. Voltage values were measured with an a-c voltmeter. The rapid drop in dielectric strength with increasing temperature is not explained but is probably due to the aluminum diffusing into the copper.

3. Frit-Resin Coatings

Continuous lengths of 0.0201 inch anodized-aluminum-clad copper wire were coated by pulling the wire around a pulley submerged in a composition consisting of 100 grams of 3419 frit, 50 milliliters of Dow Corning Resin 806A and 10 milliliters of toluene. The wire was passed from the frit-silicone resin container through a curing oven at 480° F and then to the take up spool. This resulted in a sandy coating with very little abrasion resistance. Tension on the feed spool was applied by a ratchet arrangement with the result that the wire traveled with a jerking motion. This caused the frit-resin to bead up on the wire, resulting in an uneven coating over the length of the wire. The wire dipping into the frit-resin and traveling around a pulley produced a coating which was not concentric.

TABLE VI

DIELECTRIC CONSTANT AND DISSIPATION FACTOR OF
ETHYL-SILICATE-SEALED ANODIZED WIRES DETERMINED BY GEORGIA TECH

Coating Number	Type of Anodizing	Dielectric Constant	Dissipation Factor
34	Phosphoric	1.42	2.42
35	"	2.89	1.47
40	"	2.79	1.87
42	"	4.48	1.75
Average	"	2.89	1.87
65-1	Sulfuric Acid-Magnesium Chloride	5.12	21.10
65-2	"	6.92	23.90
65-3	"	13.55	44.70
65-4	"	5.36	26.40
65-5	"	4.08	22.60
Average	"	7.01	27.74

TABLE VII

DIELECTRIC CONSTANT AND DISSIPATION FACTOR OF
ETHYL-SILICATE-SEALED ANODIZED WIRES DETERMINED BY THE UNIVERSITY OF ILLINOIS

Sample No.	Frequency (Kc) 0.4 K	0.4 D	10.0 K	10.0 D	100 K	100 D
34-1	Shorted					
34-2	Off-scale		11.23	40.3	7.35	16.50
34-3	Shorted					
34-4	Shorted					
34-5	Shorted					
35-1	6.45	6.48	5.20	2.70	4.95	1.63
35-2	5.42	3.85	4.85	1.52	4.70	1.07
35-3	Off-scale		14.80	54.00	8.05	19.50
35-4	5.22	4.64	4.90	2.00	4.82	1.35
35-5	31.40	57.20	9.07	13.80	7.18	4.40
40	Six samples, all shorted					

TABLE VIII

DIELECTRIC STRENGTH MEASUREMENTS
ON ETHYL-SILICATE-SEALED ANODIZED WIRES
DETERMINED BY THE UNIVERSITY OF ILLINOIS

Wire Sample No. 34
Coating thickness 0.00026 Inch

Temp. (°F)	Trial Number 1	2	3	4	5	6	7	8	9	10
	Breakdown Voltage									
91	550	400	400	250	550	300	250	300	0	350
200	300	450	340	500	300	300	400	340	230	300
400	350	330	250	240	250	350	290	200	150	340
600	100	0	250	290	250	300	350	60	50	190
800	100	20	170	40	0	0	20	20	0	10
900	50	0	0	0	0					

Wire Sample No. 35
Coating thickness 0.00046 Inch

Temp. (°F)	Trial Number 1	2	3	4	5	6	7	8	9	10
	Breakdown Voltage									
84	450	500	300	350	320	250	320	300	350	300
200	260	310	400	380	450	290	310	290	410	330
400	280	400	300	410	350	300	340	340	420	350
600	210	20	90	320	330	270	300	290	350	320
800	40	0	0	350	30	50	50	0	300	50

Wire Sample No. 40
Coating thickness 0.00033 Inch

Temp. (°F)	Trial Number 1	2	3	4	5	6	7	8	9	10
	Breakdown Voltage									
96	200	250	340	250	200	300	400	20	310	140
200	350	300	280	310	290	330	300	280	330	310
400	330	290	300	250	300	300	280	280	290	280
600	280	20	40	290	50	100	140	200	0	300
800	0	0	0	0	0					

To obtain smoother, more concentric coatings a vertical arrangement of the equipment was made and tension on the feed pulley was changed so that the wire would feed smoothly. A settling problem which was encountered with the vertical column of frit-resin was eliminated by the addition of a motor-driven stirrer in the column. (See Figure 6.)

Sandy coatings produced with the above composition prompted a study to obtain the proper viscosity and composition of coatings to apply to anodized wires. The coatings given in Table IX were made up to be checked for cured and fired properties.

TABLE IX

FRIT-RESIN COMPOSITIONS TESTED
FOR CURING AND FIRING PROPERTIES OF COATINGS

Composition	806 A Resin (As Recieved) (Gm)	3419 Frit (Gm)	Toluene (Ml)
30-1	50	100	10
30-2	65	100	10
30-3	70	100	10
30-4	40	100	10
30-5	30	100	10
30-6	10	100	10

These coatings were applied to short lengths of wire and to strips of enameling iron and cured at 480° F for one hour. All coatings on strip and wire came out relatively smooth and had good adherence and abrasion resistance. All coatings were fired to 1400° F. Coatings 30-1, 30-2, and 30-3 blistered and peeled from the substrate. Coatings 30-4 and 30-5 did not completely fuse and could be scraped from the metal. Coating 30-6 fused to the metal and resembled a normal porcelain enamel ground coat. Since all of the coatings tested seemed to cure properly at 480° F for one hour, it was concluded that the wire coating was not being cured properly in the continuous operation.

Of the coatings tested 30-6 seemed to be the most suitable for application to wire since it had sufficient resin to bind to the substrate to which applied and upon firing produced the smoothest coatings. The viscosity of each of the coatings tested in Table IX were measured with a Brookfield viscometer and appears in Table X.

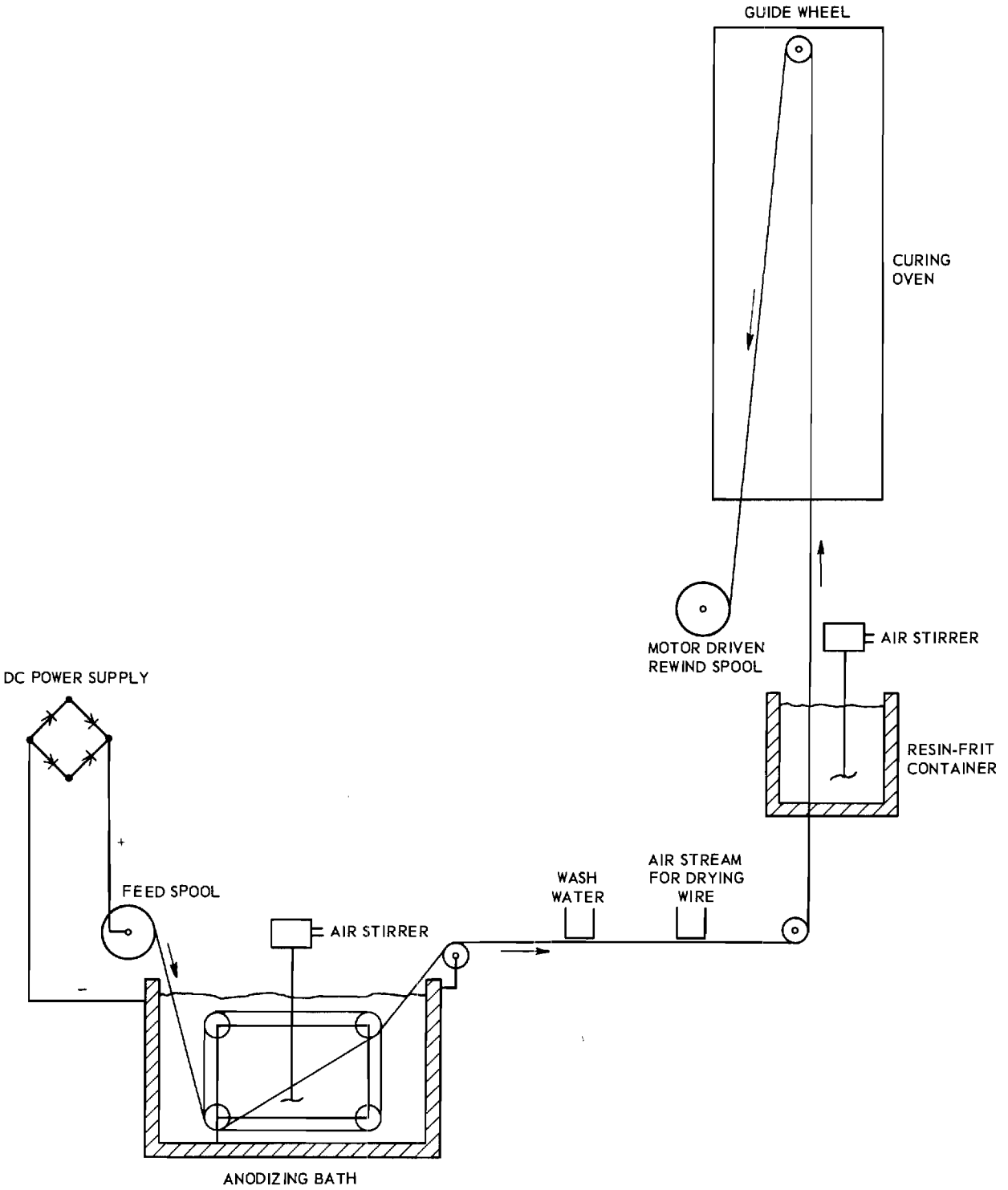

Figure 6. Schematic Sketch of Equipment for Continuously Anodizing and Coating Wire with Frit-Resin Coatings.

TABLE X

VISCOSITY OF FRIT-RESIN COMPOSITIONS

Composition	Viscosity (Centipoise)
30-1	160
30-4	190
30-5	900
30-6	1100

With the exception of coating 30-6 all coatings applied to the wire were too thin; therefore, a new series of frit resin coatings were prepared. This study appears in Table XI.

All coatings in Table XI were applied continuously to anodized-aluminum-clad copper wire or bare copper wire by pulling the wire vertically through a container of frit resin at a speed of 4 inches per minute and then through a curing oven set to maintain a temperature of 480° F. All frit resin slips were adjusted to a viscosity of 900 to 1100 centipoise by adding or deleting toluene from the mix.

Coatings through 53-3 all had a rough surface, poor abrasion resistance and poor flexibility. Wire coatings 66-1 through 66-5 had better flexibility and dielectric properties than any of the wires previously tested. From the results of this study and the studies with ethyl silicate eight additional samples of wire were continuously coated and sent to the University of Illinois for inclusion in their testing program on wire. The composition of the coatings sent to the University of Illinois appear in Table XII. The frit-resin slips applied to the wires listed in this table were more viscous than the coatings listed in Table XI. This resulted in slightly thicker coatings. The results of the electrical measurements on these wires appear in Tables XIII through XV. The best results were obtained with coatings 67-6 and 67-9, therefore, a complete testing program was carried out on these wires. The other wires had poor properties so only room temperature dielectric constant and dissipation factor were measured.

3. Aging of Aluminum-Clad Copper Wire

Considerable difficulty has been encountered in completely converting all of the aluminum on the aluminum-clad copper wire to alumina. Above 1000° F this aluminum diffuses into the copper even with nickel or silver present as a barrier layer between the two metals. This diffusion results in a reduction of the electrical conductivity of the copper and causes the wire to become very brittle. To determine the maximum operating temperature of this wire when sealed with (1) silicone resin, (2) frit resin and (3) ethyl silicate, the following work was carried out.

TABLE XI

PROPERTIES OF FRIT-RESIN COATINGS

Wire Coating	Type of Substrate	Frit-to-Resin Ratio	Thickness of Coating (In. x 10^{-3})	Mandrel-to-Wire Ratio at which Coating Spalled	Dielectric Constant	Dissipation Factor (o/o)
52-1	Sulfuric Anodized	10:1	2.27	<25:1	6:00	1.44
52-3	Phosphoric Anodized	3:1	2.52	<25:1	5.90	0.99
52-5	Phosphoric Anodized	1:1	4.93	<25:1	6.28	0.84
52-6	Phosphoric Anodized	2:1	2.26	<25:1	4.67	0.91
52-8	Phosphoric Anodized	Resin Only	2.32	<25:1	9.21	0.49
53-1	Bare Copper	10:3	1.06	<11:1	4.03	1.98
53-3	Bare Copper	2:1	2.77	44:1	11.30	3.00
66-1	Sulfuric Acid-Magnesium Chloride Anodized	1:1	2.10	<13:1	3.30	1.98
66-2	"	1:1.5	2.00	<13:1	2.43	1.44
66-3	"	1:2	1.80	<13:1	4.66	1.17
66-4	Sulfuric Acid Magnesium Chloride	1:2.5	2.15	<13:1	2.80	1.68
66-5	"	1:3	0.89	<13:1	2.20	0.76

TABLE XII

COMPOSITION OF COATINGS SENT TO THE UNIVERSITY OF ILLINOIS

Coating Number	Frit-to-Resin Ratio	Wire Speed (In./Min.)	Thickness of Coating (In. x 10^{-3})
67-1	1:3	1.6	4.60 - 7.10
67-2	1:3	4	2.70
67-3	1:2.5	1.6	2.50
67-4	1:2.5	4	4.60
67-6	1:2	4	2.10
67-7	Ethyl Silicate Only	4	0.44
67-8	Anodized Only	-	1.03
67-9	Ethyl Silicate +1:2	4	1.80

Ten foot lengths of 0.0201-inch anodized-aluminum-clad-copper wire were sealed by each of the above methods and wrapped on one-inch outside diameter glass mandrels. The two ends of each wire were left free and the resistance of each length of wire measured. Three 2-foot lengths were cut from each continuously coated wire in order to check continuity, dielectric constant and dissipation factor of the wire.

All samples were placed in a furnace at 450° F for 250 hours. At the end of 250 hours the resistance, dielectric constant and dissipation factor were determined from measurements made on each wire. The wires were then returned to the furnace for an additional 250 hours at 600° F and dielectric measurements then made. The above procedures were again repeated after 250 hours at 800° and 1000° F. After 250 hours at 1000° F the wire had become too brittle to handle while making electrical measurements; therefore, only the data through 800° F are reported in Tables XVI - XVIII. Figure 7 shows the effect of temperature on resistance of the wire. It can be seen from these tables and from Figure 7 that anodized wire sealed with silicone resin, frit-resin or ethyl silicate is capable of operating for many hours at 600° F. It may be possible to use this wire at 800° F, however, the increased dissipation factors may limit its use. The rapid increase in dissipation factor after heating at 800° F for 250 hours may be due to burn out of the resin binder and to the diffusion of aluminum into the copper as shown by the increased electrical resistance of the wire.

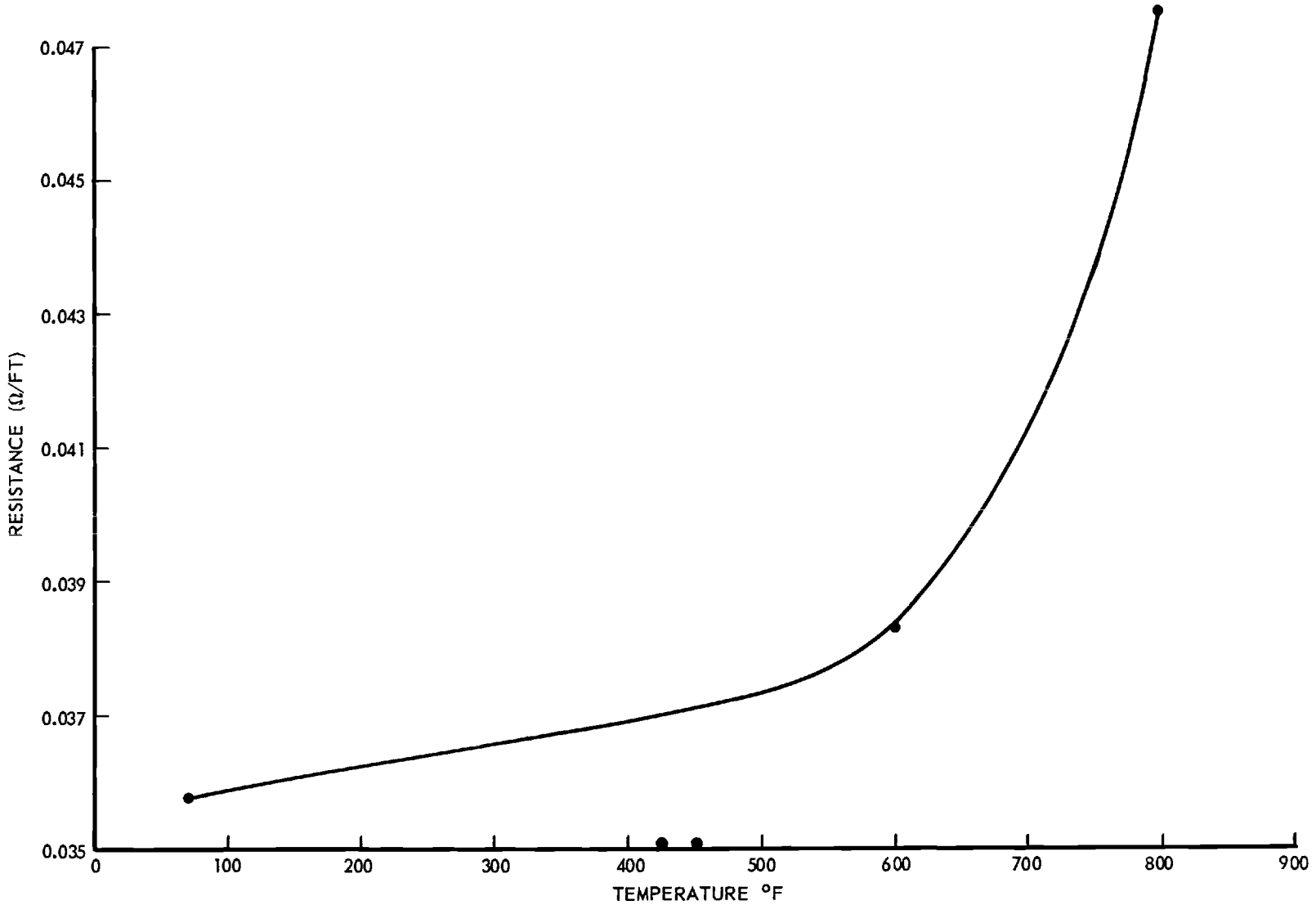

Figure 7. Average Resistance Increase with Temperature for Sealed Anodized Aluminum-Clad Wires.

TABLE XIII

INSULATED WIRE DESIGNATED 67-6

Insulated Wire Nominal Outside Diameter = 0.0241 Inch
Coating Thickness = 0.00207 Inch (Measurement Made by Georgia Tech)
Frit-to-Resin Ratio = 1:2, Wire Speed = 4 Inches/Minute

Part A. Breakdown Voltage at Elevated Temperatures

Mandrel Diameter = 2.24 Inches
Ratio of Mandrel Diameter to Nominal Coated Wire Diameter = 93:1
Total Tension on Wire to Assure Contact
with Silver Electrode = 23.4 Grams

Temperature (° F)	Breakdown Voltage (60 Cycles, RMS) Mean	Median	Range
75	295	325	0-350
200	302	300	200-300
400	244	250	200-280
600	215	220	150-280
800	194	200	120-250
1200	0	0	0

Part B. Dielectric Constant and Dissipation Factor at Room Temperature

Sample No. 1, 0.8-Inch Length, 0.00207-Inch-Thick Insulation			Sample No. 2, 0.9-Inch Length, 0.00207-Inch-Thick Insulation		
Frequency (Kc)	Dissipation Factor (o/o)	K	Frequency (Kc)	Dissipation Factor (o/o)	K
0.4	0.44	3.46	0.4	0.52	3.46
10.0	0.30	3.26	10.0	0.50	3.36
100.0	0.30	3.12	100.0	0.30	3.36

TABLE XIV

INSULATED WIRE DESIGNATED 67-9

Insulated Wire Nominal Outside Diameter = 0.0233 Inch
Coating Thickness = 0.00176 Inch (Measured by Georgia Tech)
Ethyl Silicate Coated, Frit-to-Resin Ratio = 1:2, Wire Speed = 4 Inches/Minutes

Part A. Breakdown Voltage at Elevated Temperature

Mandrel diameter = 2.24 Inches
Ratio of Mandrel Diameter to Nominal Coated Wire Diameter = 96:1
Total Tension on Wire to Assure Contact
with Silver Electrode = 23.4 Grams

Temperature (°F)	Breakdown Voltage (60 Cycles, RMS)		
	Mean	Median	Range
82	250	250	200-300
200	233	225	150-300
400	232	240	160-300
600	239	225	200-290
800	243	240	100-400
1000	202	210	0-500

Part B. Dielectric Constant and Dissipation Factor at Room Temperature

Sample No. 1 2.9-Inch Length 0.00176-Inch-Thick Insulation			Sample No. 2 3.4-Inch Length 0.00176-Inch-Thick Insulation		
Frequency (Kc)	Dissipation Factor (o/o)	K	Frequency (Kc)	Dissipation Factor (o/o)	K
0.4	1.32	4.84	0.4	7.6	5.10
10.0	2.2	3.86	10.0	2.5	4.14
100.0	1.2	3.60	100.0	1.7	3.84

ROOM TEMPERATURE DIELECTRIC CONSTANT AND DISSIPATION FACTOR FOR WIRES: 67-1, 67-2, 67-3, 67-4, 67-7, and 67-8

Sample No.	Frit-to-Resin Ratio	Wire Speed (In./Min)	Frequency (Kc)	Dissipation Factor (o/o)	K	Length (Inches)	Insulation Thickness (Inches)
67-1	1:3	1.6	0.4	1.88	15.00	2.4	0.00466-0.00705 (0.00585 used to calculate K).
			10.0	1.75	13.10		
			100.0	0.64	12.34		
67-1	1:3	1.6	0.4	0.86	15.20	1.1	0.00466-0.00705 (0.00585 used to calculate K).
			10.0	0.87	14.54		
			100.0	0.34	13.88		
67-2	1:3	4	0.4	0.44	3.02	2.2	0.00273
			10.0	0.27	2.88		
			100.0	0.30	2.82		
67-2	1:3	4	0.4	0.56	2.76	3.5	0.00273
			10.0	0.37	2.58		
			100.0	0.40	2.54		
67-3	1:2.5	1.6	0.4	0.90	4.66	2.95	0.00246
			10.0	0.60	4.34		
			100.0	0.50	4.26		
67-3	1:2.5	1.6	0.4	1.00	5.00	2.95	0.00246
			10.0	0.66	4.70		
			100.0	0.50	4.60		
67-4	1:2.5	4	0.4	0.28	3.04	2.5	0.00455
			10.0	0.40	2.92		
			100.0	0.40	2.80		

(Continued)

ROOM TEMPERATURE DIELECTRIC CONSTANT AND DISSIPATION FACTOR FOR WIRES: 67-1, 68-2, 67-3, 67-4, 67-7, and 67-8

Sample No.	Frit-to Resin Ratio	Wire Speed (In./Min)	Frequency (Kc)	Dissipation Factor (o/o)	K	Length (Inches)	Insulation Thickness (Inches)
67-4	1:2.5	4	0.4	0.48	3.88	2.7	0.00455
			10.0	0.40	3.72		
			100.0	0.40	3.62		
67-7	Ethyl Silicate only	4	0.4	off scale	off scale	0.7	0.00044
			10.0	23.40	30.40		
			100.0	26.50	22.00		
67-7	Ethyl Silicate only	4	0.4	off scale	off scale	0.5	0.00044
			10.0	10.40	17.80		
			100.0	17.20	20.60		
67-8	Anodized only	--	0.4	38.40	--	1.5	0.00103
			10.0	27.70	53.00		
			100.0	6.90	24.00		
67-8	Anodized only	--	0.4	off scale	--	2.6	--
			10.0	46.20	14.80		
			100.0	16.10	6.34		

D. Fluoride Coatings

An alternate type of coating which was considered for high temperature electrical insulation was a fluoride coating obtained by reacting gaseous flourine with metals at high temperatures. The use of fluoride coatings for electrical insulation at high temperatures was reported in a paper by S. S. Flaschen, Paul D. Garn and Robert W. Mason, entitled "Electrically Insulating Flexible Inorganic Coatings on Metals Produced by Gaseous Flourine Reactions". This paper was given at the 61st Annual Meeting of the American Ceramic Society on May 19, 1959.[2] The formation of fluoride films was discussed along with some of the electrical properties of the coatings formed. Samples of aluminum-clad copper wire were sent to the General Chemical Division of Allied Chemical and Dye Works for application of fluoride coatings, attempts were made to apply these coatings with 10 o/o fluorine at 450° C but embrittlement of the wire occurred in every case. It is believed that the elevated temperature involved in the process was responsible for the embrittlement rather than the fluorinating media. This again goes back to the problem of the aluminum-cladding on the copper wire being too thick, thus allowing too great a percentage of the aluminum to diffuse into the copper and causing embrittlement of the wire.

DISCUSSION

A. Base Coatings

The anodized coatings produced continuously both in phosphoric acid and sulphuric acid--magnesium chloride electrolyte were uniform and continuous. The phosphoric-acid-anodized coatings were thinner (about 0.5 mil) and somewhat more flexible than the sulfuric acid--magnesium chloride anodized coatings, (about 1 mil). Both types of anodized coatings generally had dielectric constants less than 4.5 but had high dissipation factors due to the porosity of the coatings. The refractoriness of alumina should have given these wires excellent dielectric properties at elevated temperatures, however, these properties were not measured due to the diffusion of unanodized aluminum into the copper. The anodizing operation was not precise enough to anodize accurately through the 2 mils of aluminum on the commercial aluminum-clad wire that was available for use. This resulted in the aluminum being selectively corroded in spots. The better conductivity of the exposed copper caused a current surge through the wire at these spots causing the wire to heat and break. Therefore, the andozing operation could not be controlled well enough to anodize closer than 0.3 mil to the barrier layer metal. This 0.3 mil of unanodized aluminum diffused into the copper at temperatures above 1000° F despite the fact that all wires had barrier layers of either nickel or silver. It has not been possible to obtain aluminum-clad copper wires with other barrier layer metals. Aluminum, copper, nickel and silver all have face centered cubic structures. Because of this fact they are readily soluble in each other. Possibly a better barrier layer material would be chrome or iron due to their body centered cubic structures.

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[2] S. S. Flaschen and P. D. Garn, "Inorganic Electrical Insulating Coatings on Aluminum and Copper," J. Am. Ceram. Soc. 42, 641-642 (Dec. 1959).

TABLE XVI

ELECTRICAL PROPERTIES OF SILICONE-RESIN-SEALED ANODIZED WIRE

Conditions	Run No.	Dielectric Constant	Dissipation Factor (o/o)	Resistance[+] (Ohm/Ft)
After preparation at room temperature	1	2.33	0.85	0.035
	2	2.02	0.93	0.037
	3	--	--	0.0355
After 250 Hours at 450° F	1	1.67	1.89	0.0355
	2	1.49	1.03	--
	3	1.79	2.47	--
After 250 Hours at 600° F	1	1.79	0.24	--
	2	1.55	0.81	0.0375
	3	1.71	0.49	--
After 250 Hours at 800° F	1	1.89	7.92	--
	2	2.66	10.96	--
	3	2.36	4.65	0.046

[+]Only one resistance specimen measured after each temperature increase. Resistance of specimen 2 measured after 500 hours at elevated temperatures (250 hours at 450° F and 250 hours at 600° F). Resistance of specimen 3 measured after 750 hours at elevated temperatures (250 hours at 450° F, 250 hours at 600° F and 250 hours at 800°F).

At least one manufacturer of anodized aluminum-clad copper wire claims the ability to operate close to 1900° F due to the barrier layer metal preventing diffusion. This has not been the case with anodized-aluminum-clad wire in this laboratory. Any heating of the wire above 1000° F has caused diffusion of the unanodized aluminum into the copper regardless of the barrier layer metal. Similarly the aluminum-clad wire treated by the Allied Chemical Corporation with 10 per cent fluorine at 450° C became brittle due to metal migration. It was suggested that a flash coating of nickel or silver on the copper core might prevent this, however, the wire treated had both a coating of nickel and silver applied prior to cladding the wire.

It is recommended that the desired type of aluminum-coated wire should be one with a uniform coating of aluminum 0.3 to 0.5 mil in thickness with a thin film of chrome, iron or some other barrier layer metal between the aluminum and the copper. This thinner film would allow the use of phosphoric-acid-anodizing and possibly all or at least the greater portion of the aluminum could be converted to alumina by more even anodizing.

B. Sealing Coatings

1. Colloidal Silica and Ethyl Silicate Coatings

The use of electrophoresis for deposition of colloidal silica in the pores of an anodized coating from an organic suspension of colloidal silica does not appear practical. Although the particles of colloidal silica in this suspension are small (less than 7 millimicrons) they cannot be made by electrophoresis to enter the extremely small pores of an anodized coating. On the other hand ethyl silicate a true liquid with a low surface tension can enter these small pores. By gelling a hydrolyzed solution of ethyl silicate on the anodized wire particles of silica are trapped in the pores of the coating. An effective seal with ethyl silicate was obtained on phosphoric-acid anodized wires but was not obtained with the sulfuric acid--magnesium chloride anodized wires. This was possibly due to the larger pore size of the phosphoric acid coating. The smaller pores of the sulfuric acid--magnesium chloride coating probably did not allow sufficient quantities of the ethyl silicate to enter the pores. If proper sealing can be obtained with ethyl silicate it would be preferred to frit-resin coatings. The ethyl silicate coating would not lose its flexibility upon being heated and again cooled to room temperature, and there would be no decomposition products.

2. Frit-Resin Coatings

By far the best sealing and electrical properties were obtained with frit-resin coatings. The best frit-resin coatings obtained were composed of 1 part 3419 frit to two parts 806A resin. These coatings gave low dielectric constant, low dissipation factor and good continuity of coating. Unfortunately no tests could be made on this coating above 1000° F due to the unanodized aluminum on the wire. After 750 hours at 800° F, however, this frit resin coating was still serviceable.

TABLE XVII

ELECTRICAL PROPERTIES OF FRIT-RESIN-SEALED ANODIZED WIRE

Conditions	Run No.	Dielectric Constant at 150 Kc	Dissipation Factor (o/o)	Resistance+ (Ohm/Ft)
After preparation at room temperature	1	5.45	6.61	0.0365
	2	9.71	6.06	0.037
	3	5.53	6.21	0.0365
After 250 Hours at 450° F	1	4.22	1.12	0.034
	2	1.92	0.24	--
	3	3.64	1.31	--
After 250 Hours at 600° F	1	4.82	4.35	--
	2	2.78	0.64	0.039
	3	3.09	1.40	--
After 250 Hours at 800° F	1	7.97	26.69	--
	2	2.53	2.43	--
	3	3.86	3.55	0.0485

+Only one specimen measured after each temperature increase. Resistance of specimen 2 measured after 500 hours at elevated temperatures (250 hours at 450° F and 250 hours at 600° F). Resistance of specimen 3 measured after 750 hours at elevated temperatures (250 hours at 450° F, 250 hours at 600° F and 250 hours at 800° F).

TABLE XVIII

ELECTRICAL PROPERTIES OF ETHYL-SILICATE-SEALED ANODIZED WIRE

Conditions	Run No.	Dielectric Constant at 150 Kc	Dissipation Factor (o/o)	Resistance+ (Ohm/Ft)
After preparation at room temperature	1	4.23	3.07	0.036
	2	3.31	3.82	0.0355
	3	3.00	2.63	0.036
After 250 Hours at 450° F	1	2.96	2.28	0.036
	2	3.04	0.55	--
	3	3.11	0.52	--
After 250 Hours at 600° F	1	2.28	0.24	--
	2	1.92	0.66	0.0385
	3	3.54	1.60	--

(Continued)

TABLE XVIII (Continued)

ELECTRICAL PROPERTIES OF ETHYL-SILICATE-SEALED ANODIZED WIRE

Conditions	Run No.	Dielectric Constant at 150 Kc	Dissipation Factor (o/o)	Resistance[+] (Ohm/Ft)
After 250 Hours at 800° F	1	3.71	24.69	--
	2	2.58	7.12	--
	3	3.08	5.93	0.048

[+]Only one specimen measured after each temperature increase. Resistance of specimen 2 measured after 500 hours at elevated temperatures (250 hours at 450° F and 250 hours at 600° F). Resistance of specimen 3 measured after 750 hours at elevated temperatures (250 hours at 450° F, 250 hours at 600° F and 250 hours at 800° F).